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October 1995

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Flash Pyrolysis and DIN 53 436 Experiments

Klaus Haahr Jørgensen & Lene Smith-Hansen

Risø National Laboratory, Roskilde, Denmark
October 1995

Abstract The report describes microscale experiments carried out by Risø National Laboratory as part of the CEC ENVIRONMENT project "TOXFIRE. Guidelines for Management of Fires in Chemical Warehouses". The objective of the project is to develop the basis for two sets of guidelines in relation to fires in chemical warehouses: Guidelines for the safety engineers to be used in accident prevention and guidelines for the fire brigade to be used if an accident nevertheless occurs.

A screening of 30 compounds (mainly pesticides) has been carried out by use of combined flash pyrolysis-GC/MS. The pyrolysis products have been identified and compared with literature data as well as with previous combustion experiments.

DIN 53 436 combustion experiments have been carried out with six pesticides: Lindane, dichlobenil, glyphosate, thiram, atrazin and dimethoate. Experiments have been carried out at 500 and 900 °C at varying oxygen concentrations, flow rates and sample load. The concentrations of combustion gases (CO_2, CO, $COCl_2$, HCl, HCN, SO_2, NO, N_2O etc.) have been measured on-line by use of FTIR and the total yields determined.

The work described in this report was sponsored by the CEC ENVIRONMENT programme (contract no. EV5V-CT93-0275)

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Contents

1 Introduction

The most important hazards from chemical storages are fires where large amounts of chemicals are involved. Toxic fire effluents might be produced and dispersed with the fire plume threatening people at the plant or in the vicinity. Also a fraction of the original substance (which e.g. could be a highly toxic pesticide) might survive the flames. Furthermore, contaminated firefighting water might be released causing harm to the environment.

In order to obtain data concerning identification and quantification of the fire products from fires in warehouses containing commercial chemicals a research project was initiated: "Combustion of chemical substances and the impact on the environment of the fire products" (The COMBUSTION project). The project was sponsored by the CEC STEP programme (contract no. STEP CT91-0109). It was initiated in July 1991 and completed in July 1994.

The project included combustion experiments of various scale with a number of selected substances such as pesticides, fertilizers, solvents and polymers. In the experiments a number of fire parameters such as toxic gas concentrations and yields, rate of heat release, ignitability and smoke production were determined. Furthermore, the particles generated from combustion of the substances were characterized. Based on the results obtained in the experiments a scaling study was carried out in order to establish a relation between bench-scale testing and real fires. Finally, an N-gas model was applied in order to assess the toxicity of the fire effluents.

The participants in the COMBUSTION project were:

- Risø National Laboratory, Denmark (coordinator).
- South Bank University, UK.
- VTT - The Technical Research Centre of Finland.
- Lund University, Sweden.
- SP - The Swedish National Testing and Research Institute.

Other problems which remain to be solved concern chemical warehouse fire prevention and mitigation. In order to study these subjects the TOXFIRE project was initiated in October 1993 with a three year project period. The project is sponsored by the CEC ENVIRONMENT programme (contract no. EV5V-CT93-0275).

The objective of the TOXFIRE project is to develop the basis for two sets of guidelines in relation to fires in chemical warehouses; guidelines for the safety engineers to be used in accident prevention, and guidelines for the fire brigade to be used if an accident nevertheless occurs. The guidelines will be the outcome of a detailed and systematic study of chemical fires supplemented by experiments based on model compounds to determine important properties of the substances involved and the source characteristics and assessment of parameters of importance for fire scenarios. Also the consequences to humans and the environment of the chemical fire is included. It is obvious that the results of the COMBUSTION project are part of the basis for the TOXFIRE study.

The participants in the TOXFIRE project are:

- Risø National Laboratory, Denmark (coordinator).
- South Bank University, UK.
- VTT - The Technical Research Centre of Finland.
- Lund University, Sweden.
- SP - The Swedish National Testing and Research Institute.
- FOA - The Swedish National Defence Research Establishment.
- NERI - The Danish National Environmental Research Institute.

Figure 1 illustrates the structure of the TOXFIRE project:

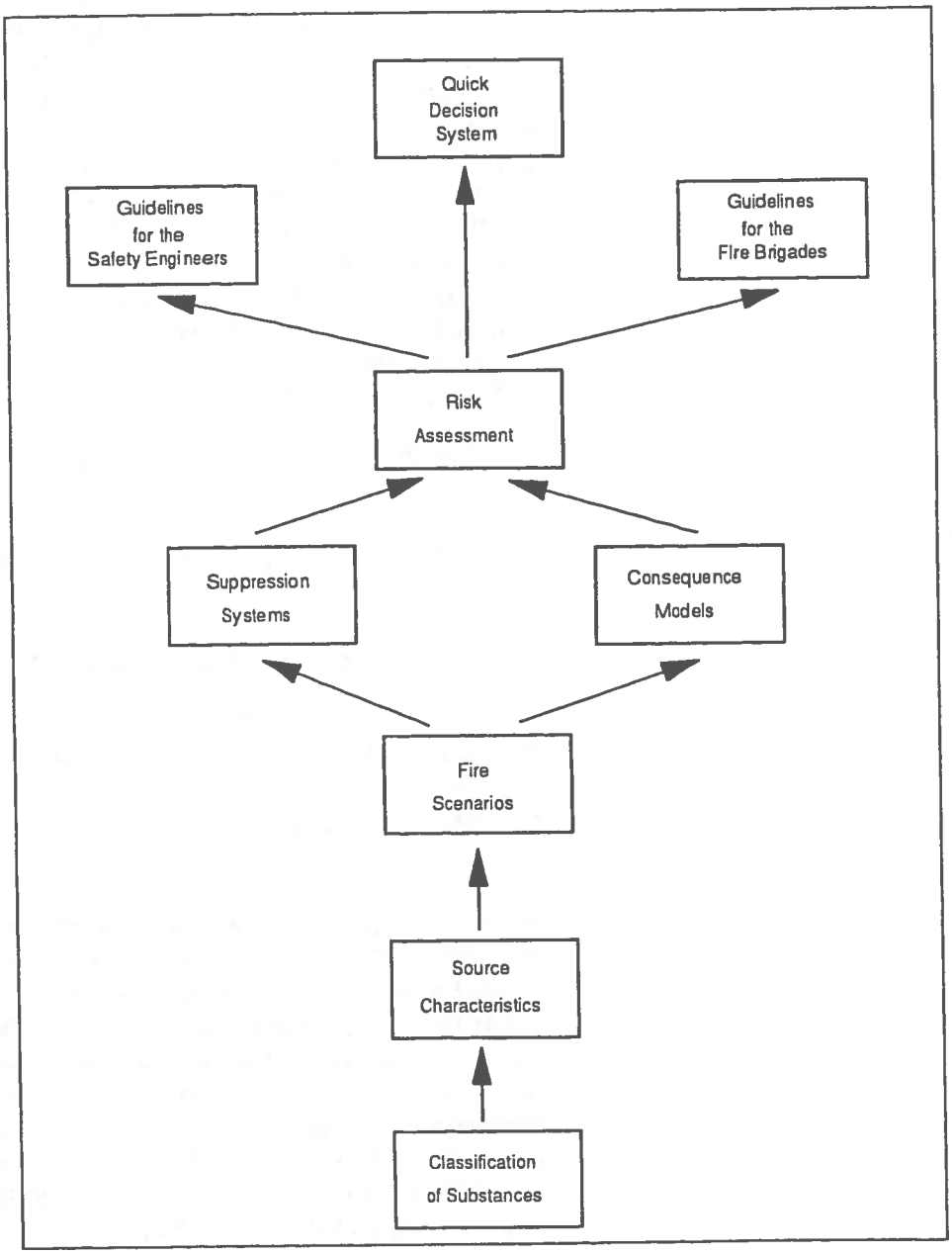


Figure 1. Structure of the TOXFIRE project.

Based on a number of parameters the substances are classified. The classification of substances requires studies and experiments of ignitability, heat release, burning rate, smoke evolution, combustion products and the influence of the packaging materials on the combustion products. The characterisation of the source uses parameters obtained by carrying out combustion experiments of various scale and by studying the effects of scaling. In addition, the fire scenarios are characterized by the degree of ventilation, the packaging materials, the stacking of the materials and the response of the building. Also the suppression is an important parameter, i.e. active and passive suppression and the fire brigade tactics. The consequences to humans as well as the environment are assessed. Finally, existing modelling methods used for risk assessment are studied, along with the handling and prevention of the accidents. These investigations are leading to development of the basis for guideline documents for the safety engineers and the fire brigades. In parallel also a quick decision system to be used by the fire chief in case of a chemical fire is developed.

The project comprises the following tasks:

- Screening of substances by flash pyrolysis and DIN 53 436 experiments.
- Cone calorimeter experiments.
- Medium-scale (model-scale) experiments.
- Indoor large-scale underventilated fire tests.
- A study of the effects of storage configurations and of fire spread models.
- Sampling and analysis of dioxins.
- A study of the consequence models for health hazards.
- A study of the consequence models for ecotoxicological effects.
- Development of a quick decision system.
- Development of a basis for guidelines for safety engineers.
- Development of a basis for guidelines for fire brigades.

The present report contains the results of the screening of substances by flash pyrolysis and the DIN 53 436 combustion experiments. These experiments were carried out by Risø National Laboratory.

2 Compounds

A number of criteria has been set up in order to select a reasonable collection of chemical compounds for the investigations. These criteria are:

- The pesticides already tested in the COMBUSTION project should be included.
- A reference substance (a polymer) should be included.
- Different functional groups and heteroatoms should be represented.
- Pesticides used/sold in large amounts (in Denmark) should be included.
- Highly toxic compounds and/or compounds expected to generate highly toxic fire effluents should be included.
- Compounds covered by the Seveso Directive should be included.

The following 30 compounds were chosen:

- Glyphosate (N-(phosphonomethyl)glycine)
- Parathion-methyl (O,O-dimethyl-O-p-nitrophenyl-phosphorothioate)
- Azinphos-methyl (O,O-dimethyl-S-[(4-oxo-1,2,3-benzotriazin-3(4H)-yl)-methyl]-phosphorodithioate)
- Dimethoate (O,O-dimethyl-S-(N-methylcarbamoylmethyl)-phosphorodithioate)
- Malathion (S-(1,2-dicarbethoxyethyl)-O,O-dimethyl-phosphorodithioate)
- Dichlorvos (O,O-dimethyl-O-(2,2-dichlorovinyl)-phosphate)
- Chlorfenvinphos (O-2-chloro-1-(2,4-dichlorophenyl)-vinyl-O,O-diethylphosphate)
- Carbophenothion (O,O-diethyl-S-4-chlorophenylthiomethyl-phosphorodithioate)
- Dialifos (O,O-diethyl-S-(2-chloro-1-phthalimidoethyl)phosphorodithioate)
- Lindane (1α,2α,3β,4α,5α,6β-hexachlorocyclohexane)
- MCPA (2-methyl-4-chlorophenoxyacetic acid)
- MCPB (2-methyl-4-chlorophenoxybutyric acid)
- Dieldrin (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-endo,exo-1,4:5,8-dimethanonaphthalene)
- Chlormequat chloride (2-chloro-N,N,N-trimethylethanaminium chloride)
- Atrazine (6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine)
- Crimidine (2-chloro-4-dimethylamino-6-methyl-pyrimidin)
- Dichlobenil (2,6-dichlorobenzonitrile)
- Propiconazole (1-[[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]-methyl]-1H-1,2,4-triazole)
- Diuron (N'-(3,4-dichlorophenyl)-N,N-dimethylurea)

- Simazine (6-chloro-N,N'-diethyl-1,3,5-triazine-2,4-diamine)
- Cyanazine (2-[[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]amino]-2-methyl-propanenitrile)
- Carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranylmethylcarbamate)
- Cycloheximide (4-[2-(3,5-dimethyl-2-oxocyclohexyl)-2-hydroxyethyl]-2,6-piperidinedione)
- Metamitron (4-amino-4,5-dihydro-3-methyl-6-phenyl-1,2,4-triazin-5-one)
- Fenpropimorf (4-[3-[4-(1,1-dimethylethyl)-phenyl]-2-methylpropyl]-2,6-dimethylmorpholine)
- Captan (N-(trichloromethyl-thio)-4-cyclohexene-1,2-dicarboximide)
- Thiram (bis(dimethylthiocarbamoyl) disulfide)
- Juglone (5-hydroxynaphthalene-1,4-dione)
- Warfarin (4-hydroxy-3-(3-oxo-1-phenylbutyl)-coumarin)
- Nylon 66

Table 1 & 2 give some details about the selected compounds. Information about the amount sold in Denmark has been found in Miljøstyrelsen (1994).

It should be noted that in addition to the combustion products given in the tables also CO, CO_2, H_2O and (depending on the combustion conditions) organic compounds, e.g. aldehydes, are expected to be generated from all compounds.

The chemical structures of the selected compounds are shown in *figure 2-5*.

Table 1. Compounds selected for flash pyrolysis experiments.

Name	Use	Amount stored to be covered by the Seveso directive [kg]	Amount sold in Denmark 1991 [kg]	Possible combustion gases from hetero-atoms
Glyphosate	Herbicide	-	447524	NO_x HCN NH_3
Parathion-methyl	Insecticide	100	<1000	NO_x HCN NH_3 SO_2 COS CS_2 H_2S PO_x
Azinphos-methyl	Insecticide	100	1467	NO_x HCN NH_3 SO_2 COS CS_2 H_2S PO_x
Dimethoate	Insecticide	-	68148	NO_x HCN NH_3 SO_2 COS CS_2 H_2S PO_x
Malathion	Insecticide	-	12642	SO_2 COS CS_2 H_2S PO_x
Dichlorvos	Insecticide	-	4055	HCl Cl_2 $COCl_2$ PO_x
Chlorfen-vinphos	Insecticide	100	1062	HCl Cl_2 $COCl_2$ PO_x
Carbophenothion	Insecticide	100	<1000	SO_2 COS CS_2 H_2S HCl Cl_2 $COCl_2$ PO_x
Dialifos	Insecticide	100	<1000	NO_x HCN NH_3 SO_2 COS CS_2 H_2S HCl Cl_2 $COCl_2$ PO_x
Lindane	Insecticide	-	15317	HCl Cl_2 $COCl_2$
MCPA	Herbicide	-	339823	HCl Cl_2 $COCl_2$
MCPB	Herbicide	-	13713	HCl Cl_2 $COCl_2$
Dieldrin	Insecticide	-	<1000	HCl Cl_2 $COCl_2$
Chlormequat chloride	Plant growth regulator	-	161970	NO_x HCN NH_3 HCl Cl_2 $COCl_2$
Atrazine	Herbicide	-	106002	NO_x HCN NH_3 HCl Cl_2 $COCl_2$

Table 2. Compounds selected for flash pyrolysis experiments.

Name	Use	Amount stored to be covered by the Seveso directive [kg]	Amount sold in Denmark 1991 [kg]	Possible combustion gases from hetero-atoms
Crimidine	Rodenticide	100	1855	NO_x HCN NH_3 HCl Cl_2 $COCl_2$
Dichlobenil	Herbicide	-	35548	NO_x HCN NH_3 HCl Cl_2 $COCl_2$
Propiconazole	Fungicide	-	114946	NO_x HCN NH_3 HCl Cl_2 $COCl_2$
Diuron	Herbicide	-	29911	NO_x HCN NH_3 HCl Cl_2 $COCl_2$
Simazine	Herbicide	-	35023	NO_x HCN NH_3 HCl Cl_2 $COCl_2$
Cyanazine	Herbicide	-	55357	NO_x HCN NH_3 HCl Cl_2 $COCl_2$
Carbofuran	Insecticide	100	3107	NO_x HCN NH_3
Cycloheximide	Fungicide, plant growth regulator	100	<1000	NO_x HCN NH_3
Metamitron	Herbicide	-	364276	NO_x HCN NH_3
Fenpropimorf	Fungicide	-	339502	NO_x HCN NH_3
Captan	Fungicide	-	45166	NO_x HCN NH_3 SO_2 COS CS_2 H_2S HCl Cl_2 $COCl_2$
Thiram	Fungicide	-	34047	NO_x HCN NH_3 SO_2 COS CS_2 H_2S
Juglone	pH indicator	100	<1000	-
Warfarin	Rodenticide	100	<1000	-
Nylon 66	Polymer	-	-	NO_x HCN NH_3

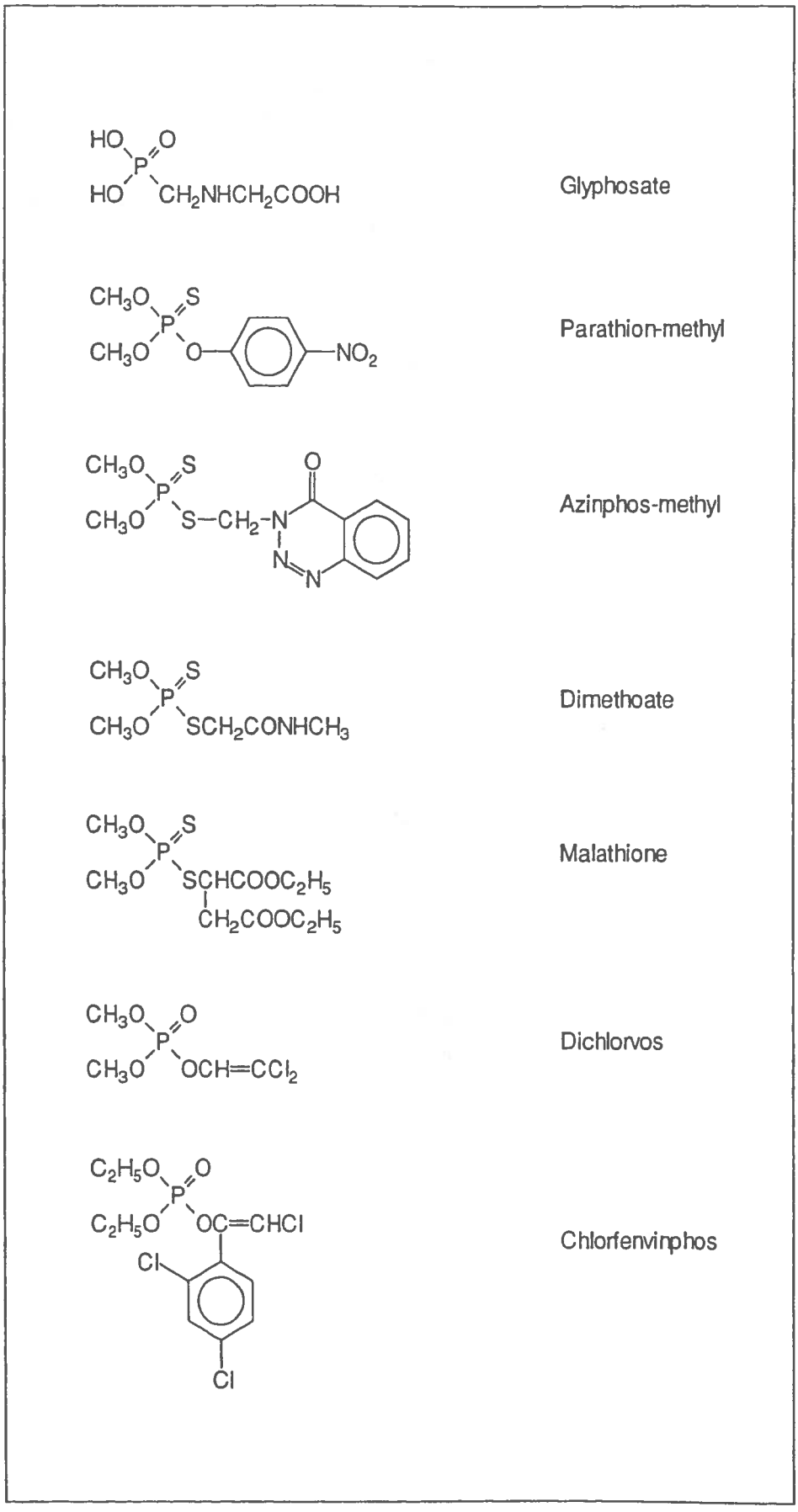
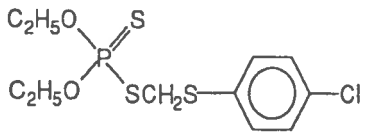
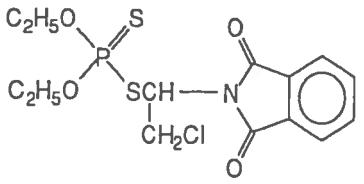


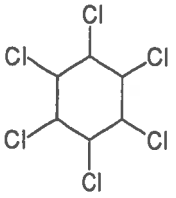
Figure 2. Chemical structure of compounds from table 1.



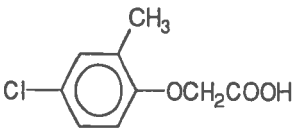
Carbophenothion



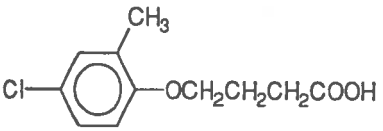
Dialifos



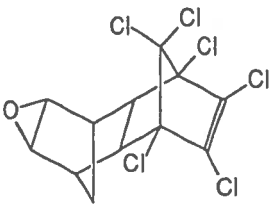
Lindane



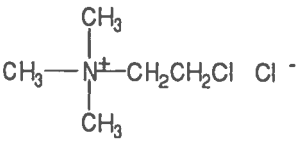
MCPA



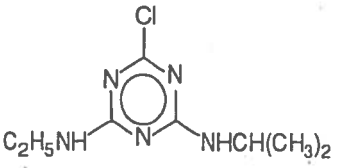
MCPB



Dieldrin



Chlormequat Chloride



Atrazine

Figure 3. Chemical structure of compounds from table 1.

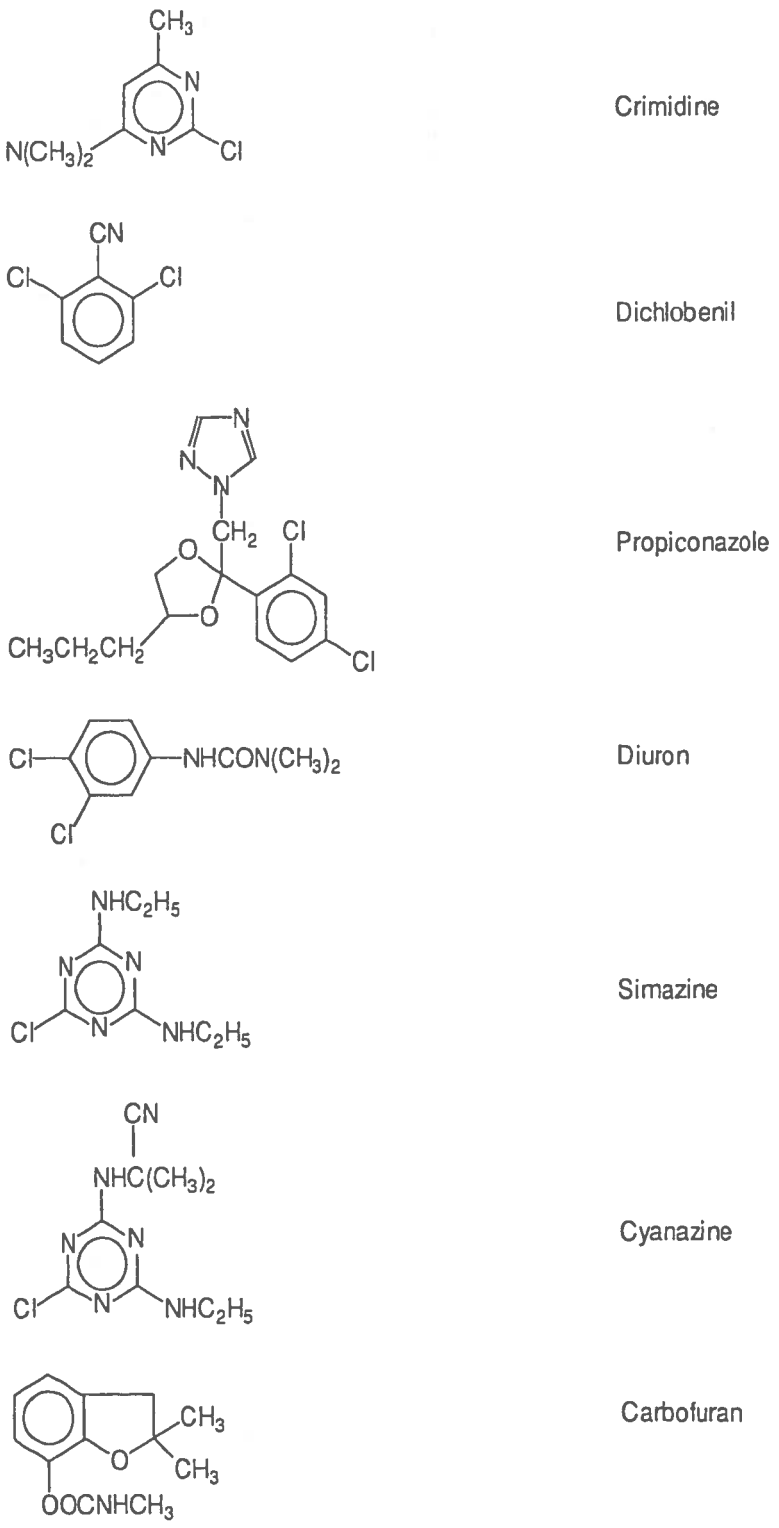


Figure 4. Chemical structure of compounds from table 2.

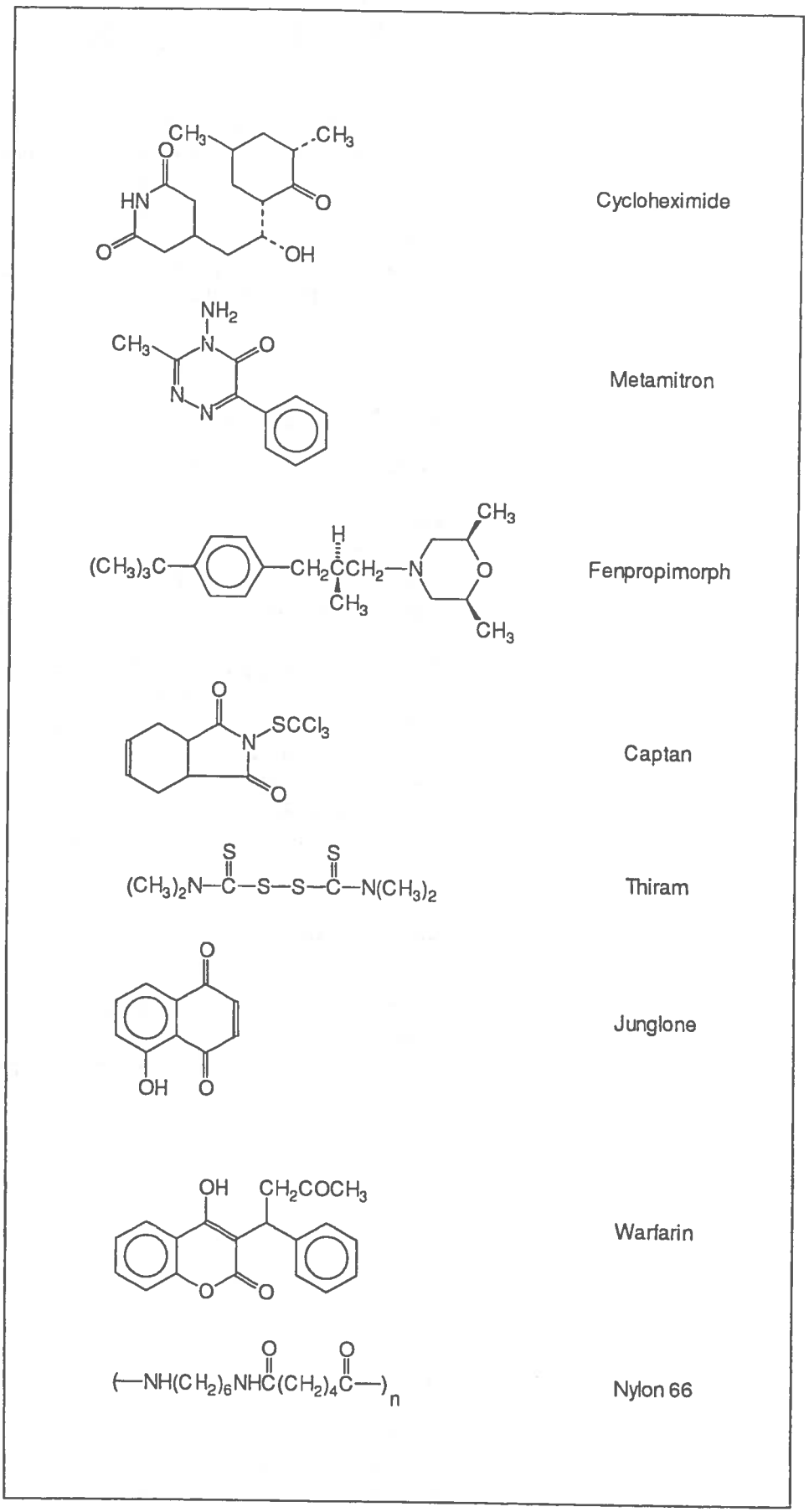


Figure 5. Chemical structure of compounds from table 2.

3 Flash pyrolysis experiments

Combined flash pyrolysis-GC/MS experiments were carried out in order to give information on the type and amounts of products from thermal decomposition. Some of these products are expected to survive a flame and will therefore be of importance, in particular in a fire under oxygen deficient conditions. Such a fire is expected to represent the worst case situation with respect to production of toxic organic decomposition products. The advantages of this method is that it is rather quick and that very little substance is required while the drawback is that information is obtained on *decomposition* rather than *combustion* products.

3.1 Experimental

The flash pyrolysis experiments were carried out using a PYROLA-85 foil pulse pyrolyzer connected to a Varian Saturn II GC/MS system. The method is described in Christiansen et al (1993). Compounds subjected to pyrolysis were placed on a platinum foil in the pyrolysis chamber (operated at 150 °C) in a helium flow connected to the GC/MS system. This was left for about 5 min prior to pyrolysis to ensure complete exclusion of air. Initially, the compounds already tested in the COMBUSTION project were pyrolyzed at 500-900 °C for 2 s. The greatest variety of pyrolysis products was seen at the highest temperatures while the main effect observed at the lowest temperatures was an evaporation of the compound subjected to pyrolysis. As most of the products from lower-temperature experiments were also seen at high temperatures it was decided to carry out pyrolysis experiments only at 900 °C.

The identification of the pyrolysis products is based on comparisons with a WILEY 5 library of standard mass spectra.

3.2 Results

Below follows the pyrolysis products identified by GC/MS from the selected compounds. In most cases not *all* products were identified and the total number of products therefore usually is somewhat larger than indicated by the lists. The products have not been quantified. However, the compounds present in the largest amounts have been determined on basis of the peak areas in the total ion chromatograms. These "major compounds" are marked with "*".

Glyphosate

benzene
pyrazine and/or pyrimidine
pyridine
toluene
pyridineamine*
methyl-1H-pyrrole
methylpyridine
dimethylbenzene and/or ethylbenzene
dimethylpyridine and/or ethylpyridine
benzenediamine*

ethylpyrazine
dimethyl-1H-pyrrole
methyl-ethylpyrazine
trimethylpyridine
trimethyl-1H-pyrrole*
methyl-propylpyrazine
ethyl-dimethylpyrazine and/or diethylpyrazine
methyl-propenylpyrazine
pyridinediamine
2,3,4,5-tetramethyl-1H-pyrrole*
ethyl-trimethyl-1H-pyrrole
dimethylindolizine
dimethylindole

Parathion-methyl

4-nitro-phenol*
phosphoric acid dimethyl-4-nitro-phenylester*
parathion-methyl*
1-methoxy-4-(1- or 2-propenyl) benzene

Azinphos-methyl

carbon disulfide*
benzene*
dimethyl disulfide
dithiapentane
toluene
phosphoric acid dimethyl ester
ethyl-benzene and/or dimethyl-benzene
ethynylbenzene
2,4-dithiapentane
styrene
phosphoric acid trimethyl ester
benzaldehyde
benzene carbothioic acid and/or diphenyl ethane dione
benzene thiol*
benzonitrile*
trithiolane
phosphorothioic acid, O,O,O-trimethyl ester
phenol
O,O-dimethyl phosphoramidothioate
1H-indene, ethynyl methyl benzene and/or propynyl benzene
benzene acetonitrile, methyl-benzonitrile and/or methyl isocyanobenzene
alpha-oxo-benzene acetonitrile
methyl-thiobenzene
phosphorothioic acid, O,O,S-trimethyl ester
benzoic acid hydrazide
benzoxazole
ortho-ethyl benzonitrile
2-hydroxy benzonitrile
phosphorodithioic acid, O,O,S-trimethyl ester*

quinoline and/or isoquinoline
azulene and/or naphthalene
benzonitrile derivative
benzothiophene
benzisothiazole and/or benzothiazole
aminobenzonitrile
1,2-benzisothiazole
benzothiazole
N-phenyl formamide
2-aminobenzonitrile, 1H-benzimidazole, 1,3-benzodiazole and/or 1H-indazole
tris(methylthio)methane
1,3,5-trithiane
benzenecarbothioic acid
isocyano-methoxybenzene
mercaptobenzonitrile
1H-indole
benzene dicarbonitrile
benzoic acid hydrazide
benzoic acid, 2-(methylamino) methylester
1-methyl-1H-indole-2,3-dione
benzonitrile derivative
diphenyl ethane dione and/or benzoic acid phenylester
ortho-tolyl isothiocyanate
benzoic acid derivative
biphenyl and/or ethenyl naphtalene
methylene bisbenzene
1H-isoindole-1,3(2H)-dione
sulphur
phosphorodithioic acid derivative
benzene carbodithioic acid methylester
2,3-dithiaindanone and/or 3H-1,2-benzodithiol-3-one
1,2,3-benzotriazin-4(3H)-one derivative and/or 1,2,3-benzotriazin-4(1H)-one derivative
thio bisbenzene
isocyanobenzene derivative and/or benzonitrile derivative
N,N-diphenyldizine and/or diphenyl methanone
diphenyl phosphinothioic acid derivative and/or phosphorodithioic acid derivative
phenylpropanone
O,O-dimethyl-S-[(4-oxo-1,2,3-benzotriazin-3(4H)-yl)methyl] phosphorothioate*
dibenzothiophene
anthracene and/or phenanthrene
diphenylmethane thione
2,3-dithia-1-indanthione
diphenyldisulfide
azinphos-methyl*

Dimethoate

phosphoric acid trimethylester
phosphorothioic acid, O,O,O-trimethylester
phosphorodithioic acid, O,O,S-trimethylester*
dimethoate*
sulphur

Malathion

benzene
phosphorothioic acid O,O,S-trimethyl ester*
C_3-benzene
phosphorodithioic acid O,O,S-trimethyl ester*
butanedioic acid diethylester
butenedioic acid diethylester*
phosphorodithioic acid O,S,S-trimethyl ester
mercaptobutanedioic acid diethylester*
thiobisbenzene
thiaphenalene/dibenzothiophene
malathion*

Dichlorvos

benzene
toluene
styrene
phosphoric acid trimethylester
phosphoric acid 2-chloroethenyl dimethylester
dichlorvos*

Chlorfenvinphos

benzene
chlorobenzene
styrene
dichlorobenzene*
chloroethynylbenzene
dichloromethylbenzene
naphthalene, azulene and/or methylene-1H-indene
dichlorophenylacetylene*
dichlorostyrene*
(chloromethyl)-dichlorobenzene
chloronaphthalene
2,4-dichloro-1-(2-chloroethynyl)-benzene
2-chloro-1-(2,4-dichlorophenyl) ethanone*
chlorfenvinphos*

Carbophenothion

benzene
toluene
chlorobenzene
styrene
chloromethylbenzene
C_3-benzene
chloro-ethyl-benzene
chlorobenzenethiol
naphthalene, azulene and/or methylene- 1H-indene

O,O,S-triethyldithiophosphate*
2,6-bis(1,1-dimethylethyl)-4-methyl-phenol
thiodiphosphoric acid tetraethylester
phosphorodithioic acid O,O-diethyl-S-[(ethylthio)methyl]ester
bis(4-chlorophenyl)disulfide
carbophenothion*

Dialifos

benzene
toluene
ethynylbenzene
styrene
benzonitrile
ethynyl-methylbenzene and/or propynylbenzene
isocyanomethylbenzene, methylbenzonitrile and/or benzeneacetonitrile
naphthalene, azulene and/or methyleneindene
O,O-diethyl-S-ethyl phosphorothioate
quinoline and/or isoquinoline
benzo[b]thiophene
mercaptobenzonitrile, benzothiazole, bezisothiazole and/or thienopyridine
quinolinol, 2(1H)-quinolinone and/or phenyloxazole
O,O-diethyl-phosphorothioic acid derivative
1H-indene-1,3(2H)-dione
O,O-diethyl-phosphorodithioic acid derivative
2-phenylthiazole*
phthalimide*
N-vinylphthalimide*
methylnaphthalenedione*
sulphur
dialifos*

Lindane

benzene
chlorobenzene
dichlorobenzene (3 isomers)
trichlorobenzene (3 isomers)
tetrachlorobenzene (3 isomers)
tetrachlorocyclohexenes
pentachlorocyclohexenes
lindane*

MCPA

benzene*
toluene
chlorobenzene
ethylbenzene and/or dimethylbenzene
styrene
1-chloro-3-methyl-benzene*

phenol
indene, propynylbenzene and/or ethynyl-methyl-benzene
chloro-ethyl-benzene
2-methyl-phenol
chloro-ethenyl-benzene
dimethyl-phenol
5-chloro-benzofuran and/or 7-chloro-benzofuran
naphtalene and/or azulene
4-chloro-phenol
4-chloro-2-methyl-phenol*
4-chloro-2-methyl-benzaldehyde
dichloro-benzene-methanol and/or dichloro-methyl-phenol
dimethyl-chloro-phenol
bihenylene and/or acenaphtylene
dibenzofuran
2-methyl-phenoxy acetic acid
4-chloro-2-methyl-phenoxy acetic acid methyl ester
xanthene
MCPA*

MCPB

benzene
toluene
chlorobenzene
dimethylbenzene and/or ethylbenzene
styrene
1-chloro-3-methyl-benzene
benzofuran
1H-indene, propynylbenzene and/or ethynyl-methyl-benzene
chloroethylbenzene
2-methylphenol
chloroethenylbenzene
4-chloro-2-methylphenol*
dimethylchlorobenzene
phenylpropenal and/or methylbenzofuran
dichlorophenol
5-chlorobenzofuran and/or 7-chlorobenzofuran
4-chlorophenol
4-chloro-2-methyl-benzaldehyde
dichloromethylphenol
MCPB*

Dieldrin

benzene
toluene
chlorobenzene
ethynylbenzene
styrene
benzaldehyde and/or benzeneacetic acid alpha-oxo methylester
dichlorobenzene

chloro-1,3,5-cycloheptatriene
dichlorobenzene (3 isomers)
1H-indene, 1-propynylbenzene and/or ethynyl-methylbenzene
benzene methanol
naphthalene and/or azulene
trichlorobenzene (3 isomers)
methylene-1H-indene
1,1,2,3,4,4-hexachloro-1,3-butadiene
tetrachlorobenzene (3 isomers)
2-ethenyl naphthtalene and/or biphenyl
pentachlorobenzene
dichloronaphtalene
chlordene
1,2,3,4,10,10-hexachloro,1,4,4a,5,8,8a-hexahydro-endo,exo-1,4:5,8-dimethano-naphthalene*
dieldrin*
various chlorinated compounds

Chlormequat chloride

benzene*
toluene*
styrene*
ethenylpyridine
vinylpyridine, isocyanobenzene and/or benzonitrile*
$C_{10}H_{10}$
quinoline and/or isoquinoline
naphthalene, azulene and/or methyleneindene*
methylnaphthalene
biphenyl
ethylnaphthalene and/or dimethylnaphtalene
biphenylene and/or acenaphthylene
dihydroacenaphthylene
ethenylnaphthalene
isocyanonaphthalene and/or naphthalenecarbonitrile
propenylnaphthalene
$C_{14}H_{14}$
9H-fluorene
methyl-9H-fluorene
phenanthrene, anthracene and/or methylene-9H-fluorene
fluoranthene and/or pyrene

Atrazine

atrazine*

Crimidine

crimidine*

Dichlobenil

1,3-dichlorobenzene
benzonitrile
2,6-dichlorotoluene*
2-chlorobenzonitrile
trichlorobenzene
dichlobenil*

Propiconazole

chlorobenzene
styrene
chloromethylbenzene
benzonitrile and/or isocyanobenzene
dichlorobenzene*
chloroethynylbenzene
C_3-benzene
chlorobenzonitrile
dichloromethylbenzene
naphthalene, azulene and/or methylene-1H-indene
dichloroethynylbenzene*
dichlorobenzonitrile
chloronaphthalene
dichlorobenzeneacetonitrile
biphenylene and/or acenaphthylene
(chloromethyl)naphthalene
dichloronaphtalene
2-chloro-1-(2,4-dichlorophenyl)ethanone
dichlorobiphenyl
tetrachlorobiphenyl
propiconazole*

Diuron

benzene
toluene
chlorobenzene
hydroxybenzonitrile, benzoxazole and/or benzisoxazole
benzonitrile
1,2-dichlorobenzene*
isocyano-methylbenzene
chlorobenzonitrile
chlorophenylisocyanate (3-chloro and 4-chloro)*
dichloromethylbenzene
naphthalene, azulene and/or methylene-1H-indene
3,4-dichlorophenylisocyanate*
monuron
diuron*

Simazine

4,6-dichloro-N-ethyl-1,3,5-triazin-2-amine
simazine*

Cyanazine

methylenepropanedinitrile and/or butenedinitrile
methylpyridine
pyridinamine
methyl-cyclopentene
methylpropanedinitrile
vinylpyridine, benzonitrile and/orisocyanobenzene
1,4-dicyano-1,3-butadiene and/or pyridinecarbonitrile
hexenedinitrile
dicyanobenzene
$C_6H_6N_4$
6-chloro-N-ethyl-1,3,5-triazine-2,4-diamine
6-chloro-N,N'-diethyl-1,3,5-triazine-2,4-diamine (simazine)
chloroantracene, chlorophenanthrene and/or chloro(phenyl-ethynyl)benzene
cyanazine*

Carbofuran

benzene
toluene
ethylbenzene and/or dimethylbenzene
ethynylbenzene
styrene
ethyl-methylbenzene and/or trimethylbenzene
phenol
benzofuran
C_3-benzene (C_9H_{10})
methyl-ethynylbenzene and/or propynylbenzene
methylphenol
methylbenzofuran
$C_{10}H_{10}$
ethylphenol and/or dimethylphenol
naphthalene, azulene and/or methyleneindene
2-vinyl-2,3-dihydrobenzofuran
$C_8H_{10}O_2$
2,3-dihydro-2,2-dimethyl-7-benzofuranol*
methylbenzofuranone, propylbenzaldehyde and/or trimethylbenzaldehyde*
biphenyl
naphthalenediol
naphthalenol
carbofuran*

Cycloheximide

toluene
ethylbenzene and/or dimethylbenzene
styrene
phenol
2,4-dimethylcyclohexanone*
methylphenol
acetyl-dimethylphenol and/or methyl-butylphenol
cycloheximide*

Metamitron

benzene
2-butenedinitrile and/or methylenepropanedinitrile
toluene
ethylbenzene and/or dimethylbenzene
ethynylbenzene
styrene
butanedinitrile and/or methylpropanedinitrile
benzonitrile*
2-phenylaziridine
methylbenzonitrile, methylisocyanobenzene and/or benzeneacetonitrile
C_3-benzene
ethylbenzonitrile, dimethylbenzonitrile and/or methylbenzeneacetonitrile
3-phenyl-2-propenenitrile, quinoline and/or isoquinoline
naphthalene and/or azulene
benzenedicarbonitrile
aminobenzonitrile, 1H-indazole, methyl-isonicotinonitrile, 1,3-benzodiazole and/or 1H-pyrrolopyridine
biphenyl
cyanobenzeneacetonitrile, dicyanotoluene and/or 1H-indole-carbonitrile
isocyanonaphthalene, naphthalenecarbonitrile and/or 1,3,5-tricyanobenzene
9H-fluorene
acridine, phenanthridine, 9H-fluorene-9-imine, benzo[h]quinoline and/or [1,1'-biphenyl]-2-carbonitrile
1,1'-(1,2-ethynediyl)bisbenzene, methylenefluorene, anthracene, phenanthrene and/or benz(a)azulene
metamitron*

Fenpropimorf

benzene
toluene
ethylbenzene and/or dimethylbenzene
styrene
C_3-benzene
C_4-benzene
naphthalene, azulene and/or methylene-1H-indene
$C_{11}H_{12}$
$C_{12}H_{16}$
tetrahydro-trimethyl-naphthalene and/or dihydro-tetramethyl-1H-indene

tertbutyl-methyl-benzene
various aromatic hydrocarbons
fenpropimorf*

Captan

trichloromethanesulfenylchloride
benzene
benzonitrile
1H-isoindole-1,3(2H)dione
tetrahydrophthalimide*
sulphur
captan*
N-(trichloromethylthio)phthalimide*

Thiram

isothiocyanatomethane
dimethyldisulfide
dimethyltrisulfide
tetramethylurea
1,2,4-trithiolane
N,N-dimethyl-ethanethioamide
tetramethylthiourea
dimethyl-carbamodithioic acid methylester
sulphur*
1,2,3,5,6-pentathiepane
hexathiepane
tetramethylthiurammonosulfide*
thiram

Juglone

benzene
toluene
styrene
phenol
benzofuran
1,4-naphtalenedione
2H-1-benzopyran-2-one
juglone*

Warfarin

1,3-cyclohexadiene, 1,4-cyclohexadiene and/or methylcyclopentadiene
benzene*
toluene
dimethylbenzene and/or ethylbenzene
ethynylbenzene*
styrene*

phenol
benzofuran
C_3-benzenes
C_4-benzenes
2-methylbenzofuran and/or phenylpropenal
naphthalenedione
naphthalene and/or azulene
benzofuranone
C_5-benzenes
methyl-benzofuranone
ethenylbenzofuran and/or phenylfuran
indenedione
4-phenyl-3-buten-2-one*
$C_{11}H_{10}$
methylnaphthalene and/or ethylideneindene
2-phenyl-1-para-tolylethanol
biphenyl
2H-1-benzopyran-2-one
methylene bisbenzene and/or 2-methylbiphenyl
biphenylene and/or acenaphthylene
3-methyl-2H-1-benzopyran-2-one
1,1-diphenylethane
2-methyl-4H-1-benzopyran-4-one
dibenzofuran
1,2-diphenylethane
dihydrobenz[a]azulene
9H-fluorene
anthracene and/or phenanthrene
fluorene derivative
methyl-9H-fluorene
xanthene
diphenylacetylene
dihydroanthracene and/or dihydrophenanthrene
2H-furo[2,3-h]-1-benzopyran-2-one and/or psoralene
1,2-diphenylethene
phenethrol and/or diphenylketene
diphenylpropene
phenylindene, methylanthracene and/or methylphenanthrene
anthracene and/or phenanthrene derivative
phenylbenzofurane
chalcone
benzocoumarin and/or 9H-xanthen-one
phenylnaphthalene and/or 9-ethenylanthracene
phenylindene, methylanthracene, methylphenanthrene, ethylidenefluorene and/or dihydrotrindenes
phenylisocoumarin and/or phenylbenzopyrone
phenylanthracene and/or binaphthtalene

Nylon 66

A large number of aliphatic and aromatic pyrolysis products were seen. However, it was not possible to unequivocally identify the products.

3.3 Discussion

Only a limited number of references have been found concerning thermal decomposition/pyrolysis of the investigated compounds. Below follows a comparison of the data found in the literature with those obtained in the present study.

As mentioned in chapter 2, all pesticides previously tested in DIN experiments as part of the COMBUSTION project were included in the flash pyrolysis experiments: Lindane, MCPA, dimethoate, azinphos-methyl, parathion-methyl and nylon 66 (the last compound as reference). There seems to be good qualitative agreement between DIN and pyrolysis experiments, i.e. most (but not all) products identified in the DIN experiments (Smith-Hansen & Jørgensen, 1992) were also seen in the pyrolysis experiments, but in general a wider range of products were found.

Organophosphorus pesticides

In general, organophosphorus pesticides are thermally unstable and undergo reactions of isomerization, polymerization and decomposition when heated (Mac Smith & Ledbetter (1971), McPherson & Johnson (1956)). Bertoni et al (1986) reports that a slow degradation process of azinphos-methyl takes place already below 50 °C and that the thermal decomposition of this compound is almost instantaneous at 170-180 °C, resulting in a large number of products from both primary and secondary reactions. In contrast to this, Guey & Roulph (1991) only found four decomposition products from dichlorvos at 100-200 °C. Both findings are in agreement with the present study in which the number of decomposition products seem to depend on the size and stability of the substituents.

Mac Smith & Ledbetter (1971) state that the first step in the thermal decomposition of organophosphorus pesticides involves the loss of the electrophilic group bond to phosphorus. This kind of losses are observed in several of the pyrolysis experiments, e.g. 4-nitrophenol from parathion-methyl, mercaptobutanedioic acid diethylester from malathion and 2-chloro-1-(2,4-dichlorophenyl) ethanone from chlorfenvinphos.

MCPA & MCPB

The pyrolysis products from these compounds are in agreement with the general pyrolysis schemes of chlorophenoxy acids proposed by Gomez et al (1988) and decomposition products reported by Merz et al (1986).

Dichlobenil

Matuschek et al (1991) have reported that dichlobenil evaporates without decomposition at 496 K. In the pyrolysis experiments we have found several decomposition products but this is not surprising as our experiments were carried out at a higher temperature.

Diuron

Results from pyrolysis of diuron in helium atmosphere reported by Gomez et al (1982) are in excellent agreement with the present experiments except that we did not observe any anilines. This might be caused by the different residence times in the two studies. In the study by Klusmeier et al (1989) on combustion of the very similar compound metoxuron at 600-1000 °C the same types of products were seen but anilines were neither identified.

Thiram

The pyrolysis products found from this pesticide is in agreement with decomposition processes proposed by Staudner et al (1976) according to which a number of parallel and successive reactions with chain mechanisms take place.

4 Combustion experiments

The DIN 53 436 furnace (Deutsche Normen, 1981) was used for the combustion experiments. The method is considered to be relevant for simulation of non-flaming oxidative decomposition and fully developed fires (Fardell & Woolley, 1988). The experiments were carried out at 900 and 500 °C furnace temperature in order to simulate these two scenarios.

4.1 Compounds for combustion experiments

Representatives of different types of compounds were selected among the compounds subjected to flash pyrolysis. In most cases the choice was mainly based on the amounts sold in Denmark. The following compounds were chosen:

- Lindane (Sigma H-4500) was chosen as a representative of the heavily chlorinated compounds. It was suspected that such compounds could produce substantial amounts of the highly toxic gas $COCl_2$ beside the main chlorine product HCl. Experiments were carried out only at 900 °C, but with a sample load of 3, 2 and 1 g, respectively, in order to investigate the influence of the sample load on the results.
- Dichlobenil (Aldrich D 5,755-8) was chosen in order to study the production of the highly toxic HCN from a compound containing a cyano group. This compound was also selected as a possible candidate for experiments in all scales and additional experiments were therefore carried out at different flows and oxygen concentrations.
- Glyphosate was chosen because it is the pesticide sold in the largest amount in Denmark. The substance was supplied by Monsanto and consisted of 62 % glyphosate isopropylamine salt, 35 % water and 3 % isopropylamine and related impurities.
- Thiram was chosen as a representative of the compounds containing large amounts of sulphur. It was selected as the only non-phosphorus compound with this characteristic. Beside SO_2 it was anticipated that also the gases H_2S, COS and CS_2 would be produced. From a toxicological point of view these gases are important. The substance was supplied by KVK Agro A/S.
- Atrazin (Janssen 16.168.66) was chosen as a representative of the group of triazines.
- Dimethoate (supplied by Cheminova Agro A/S) was chosen as a representative of the group of organophosphorus esters. The experiments were carried out only at 900 °C, but with the pure compound as well as a formulation. The formulation consisted of: Dimethoate 408 g/l, Berol (emulgator) 50 g/l, Cyclohexanone 455 g/l, Xylene 138 g/l.

4.2 Experimental

Below follows a description of the furnace used for combustion experiments and the gas analyses carried out.

The DIN 53 436 furnace

The DIN 53 436 furnace consists of a quartz combustion tube (length 1 m, diameter 4 cm) and a movable annular electric oven enclosing a section of the tube. The substance is placed in a 40-cm quartz boat inside the tube; in the experiments reported here, samples of 1-3 g pesticide were applied. During the combustion experiment the oven moves with a speed of 1 cm/min along the tube and air enters the tube in the direction opposite to that of the oven. An airflow of 100 l/h was used in the experiments reported here except in some of the dichlobenil experiments in which the effects of reduced airflow as well as reduced oxygen concentration were examined. The method is intended to simulate steady-state conditions, since a constant production of combustion gases is approached during the experiment. The DIN 53 436 furnace is illustrated in *figure 6*.

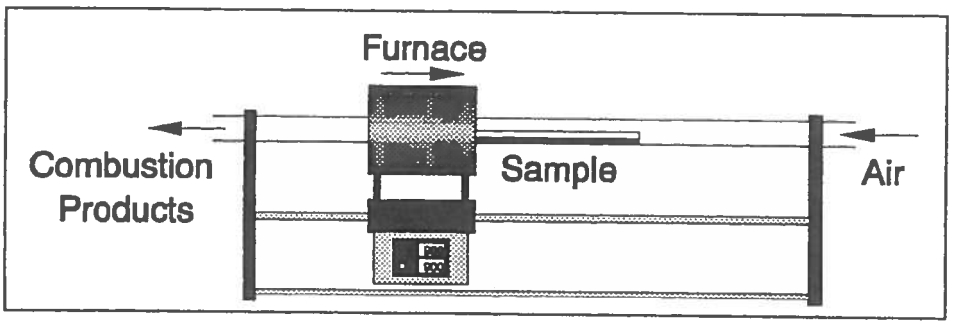


Figure 6. Combustion furnace in accordance with DIN 53 436.

As previously described (Smith-Hansen & Jørgensen, 1992), the DIN method had to be slightly modified in order to ensure a constant production of combustion gases: 24 quartz vessels were placed in the quartz boat and the pesticide was distributed approximately uniformly in the vessels. A similar procedure has been described by Einbrodt et al (1989).

FTIR gas analysis

A Bomem MB100 FTIR instrument was used for on-line gas analyses in the DIN experiments. The instrument was equipped with a multiple-pass gas cell with a pathlength of 6.4 m and a volume of 0.7 l. The sample line and the gas cell were heated to 180 °C in order to avoid condensation of combustion gases. The flow rate in the DIN experiments was not high enough to ensure the recommended (Kallonen & Mikkola, 1992) renewal of the sample in the gas cell every 10 s. However, tests with varying concentrations of calibration gases showed that accurate average concentrations were obtained under conditions similar to those in the DIN experiments; only peak values tended to be too low.

The calibration spectra were recorded with a flow of 100 l/h through the gas cell of known concentrations of single-component mixtures in nitrogen. This flow was maintained for at least five minutes before a spectrum was recorded. For each component a spectral region was selected for the calibration. In some cases, however, different regions were selected for different concentration ranges in order to obtain good predictions in the entire calibration range. The spectral regions were chosen so that the measured absorbances had a reasonable size (not too high) and interferences were avoided when possible. *Table 3* shows the concentration ranges covered by the calibrations and the spectral regions used for each range.

Table 3. Concentration ranges and spectral regions for quantification of fire gases by FTIR.

Fire gas*	Concentration range	Spectral region
CO_2	0-300 ppm	2391-2283 cm^{-1}
	300-5000 ppm	750-674 cm^{-1}
	0.5-13.6 %	800-744 cm^{-1}
		+ 732-727 cm^{-1}
CO	0-2 %	2187-2075 cm^{-1}
$COCl_2$	0-110 ppm	868-835 cm^{-1}
	110-533 ppm	1863-1791 cm^{-1}
HCl	0-1 %	2867-2696 cm^{-1}
HCN	0-1000 ppm	3373-3234 cm^{-1}
SO_2	0-350 ppm	1390-1323 cm^{-1}
	350-4000 ppm	1251-1110 cm^{-1}
	0.4-1 %	2530-2451 cm^{-1}
NO	0-544 ppm	1947-1899 cm^{-1}
N_2O	0-1 %	1284-1259 cm^{-1}

*: NO_2 was not detected in any of the DIN experiments and was therefore not included in the calibrations

The PLSplus program Version 2.1G (Galactic Industries) was used to build calibration models based on multivariate techniques. The partial least-squares algorithm used (PLS-1) has the ability to flag possible outliers as well as to model smaller spectral interferences. The integrated absorbances rather than the actual concentrations were used as input to the PLS algorithm as described by Bak & Larsen (1994, 1995) because of the nonlinearity between absorbance and concentration. This nonlinearity is mainly caused by the relatively low spectral resolution setting of the instrument (4 cm^{-1}) compared to the molecular spectral linewidth of the measured gases (~0.1 cm^{-1}). As a result of the procedure, the PLS model predictions were absorbance values which had to be converted to concentrations. This conversion was carried out by means of polynomials found by use of the fitting facilities in standard graphing software. As an example, the plot in *figure 7* shows the relation between integrated absorbances and concentrations from the CO calibration.

Interferences from H_2O, HCN and N_2O were handled by spectral subtraction: In each case, the calibration spectrum which best matched the actual concentration of the interfering component was selected before subtraction. The spectrum was selected among more than 20 calibration spectra recorded for each component in order to minimize problems related to spectral nonlinearities. For HCN and N_2O the calibration spectra were selected on basis of the PLS predictions but H_2O-spectra were selected on basis of five absorption peaks rarely affected by interferences. As can be seen in *figure 8*, spectral subtraction usually gives good results in the concentration ranges covered by the calibration spectra. Outside the calibration ranges (and occasionally even inside) the result is less satisfying. *Figure 9* shows a rather extreme case from combustion of glyphosate which contained 35% water. The water concentration was about 200% of the maximum concentration covered by the calibration.

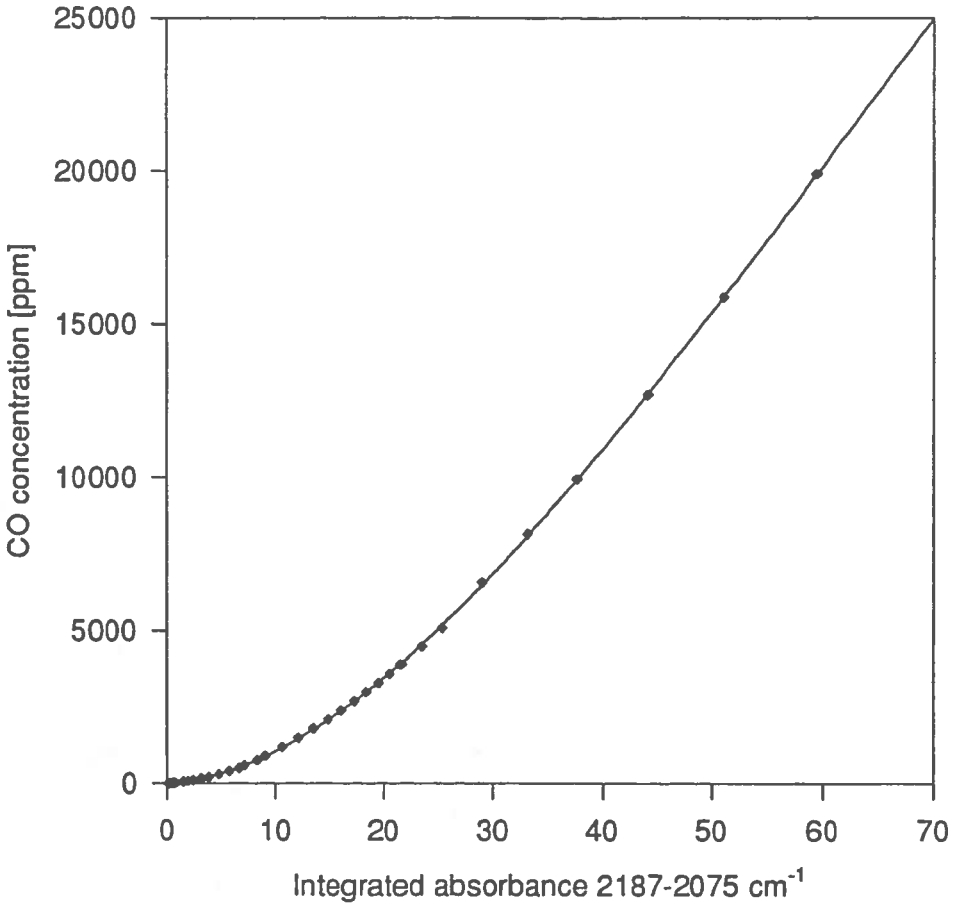


Figure 7. CO calibration - relation between absorbance and concentration. Data fitted by a polynomial of fourth order.

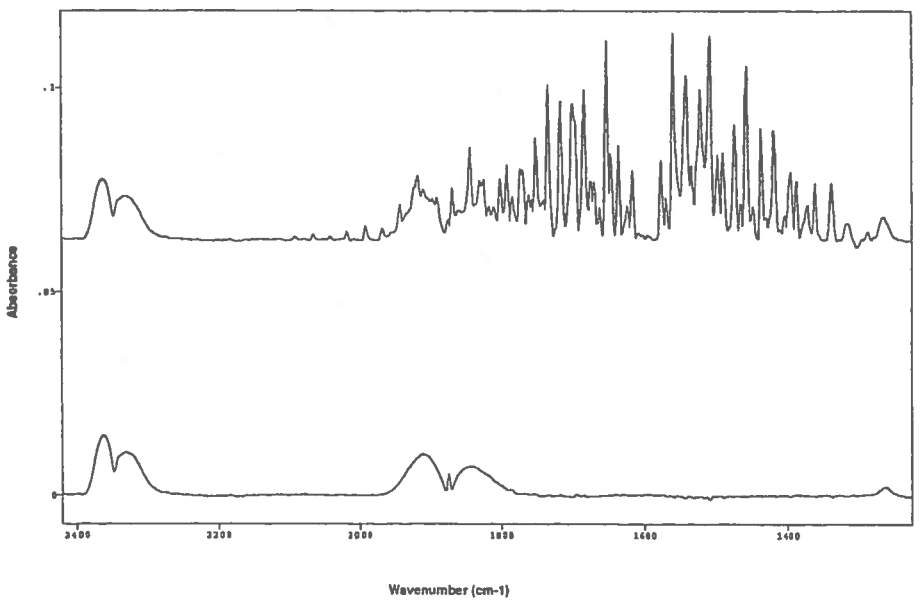


Figure 8. Spectrum of 47 ppm NO (upper) and the same spectrum after water subtraction (lower).

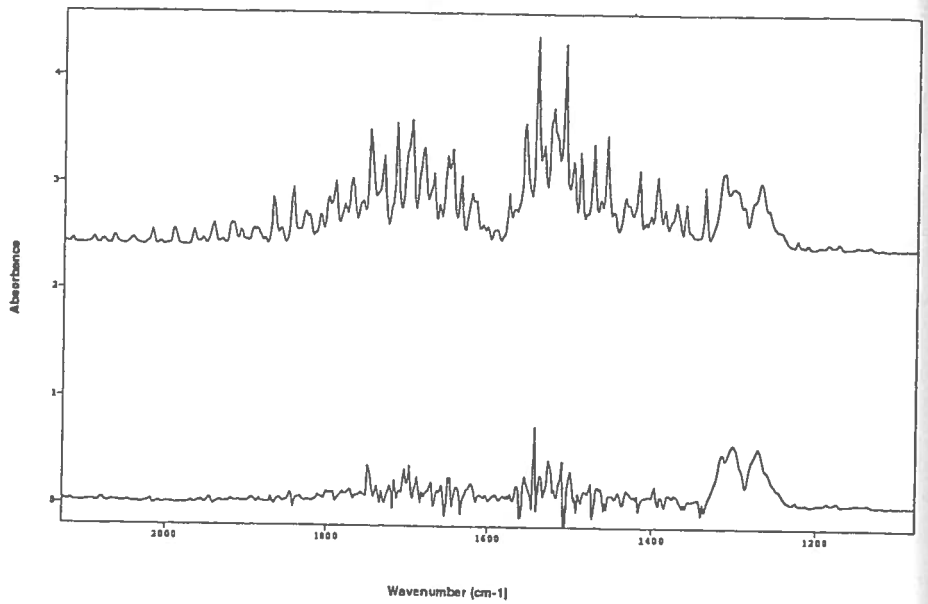


Figure 9. Spectrum from combustion of glyphosate (upper) and the same spectrum after water subtraction (lower).

Quantification on basis of spectra recorded during DIN experiments (~300 spectra pr. experiment) was automated by use of a program written in Array Basic (part of the Grams/386 software package from Galactic Industries). Results from automatic quantifications were checked by manual inspection of a number of spectra from each experiment.

4.3 Results of the FTIR measurements

Plots showing the measured concentrations as a function of time are presented in annex A. It should be noted that the concentrations shown are the uncorrected results from the automatic quantification.

On the next pages follow tables for the six substances subjected to combustion experiments containing: experimental conditions, average gas concentrations, yields (in g pr. g substance) and maximum theoretical yields. Although no calibrations were made for NH_3, CH_4, COS and CS_2, a rough estimate of the concentrations of these compounds are given in the tables when relevant. These estimates are based on a single spectrum for each compound from a library of reference spectra.

In experiments with smaller interferences the average concentrations are adjusted on basis of the manual inspection but in a few cases strong interferences only permits an upper limit to be estimated.

In some experiments calibration ranges were exceeded. In most cases, however, not more than to allow the concentrations to be reliably estimated.

Table 4. Lindane combustion gas concentrations.

Exp.	Amount	Flow	Temp.	Time	CO_2	CO	$COCl_2$	HCl
	g	l/h	°C	sec.	ppm	ppm	ppm	ppm
lin1	2.9605	100	900	2950	5989	~11000	199	>10000
lin2	1.9195	100	900	2890	2038	~8500	148	~8500
lin3	1.0629	100	900	2940	1036	4994	149	~5500

Table 5. Lindane combustion gas yields.

Exp.	CO_2	CO	$COCl_2$	HCl
	g/g	g/g	g/g	g/g
lin1	0.298	~0.349	0.022	>0.413
lin2	0.153	~0.407	0.025	~0.530
lin3	0.143	0.439	0.046	~0.630
Theoretical max.	0.908	-	-	0.752

Table 6. Dichlobenil combustion gas concentrations.

Exp.	Amount	Air/N_2-flow	Temp.	Time	CO_2	CO	$COCl_2$	HCl	HCN	NO	N_2O
	g	l/h	°C	sec.	ppm	ppm	ppm	ppm	ppm	ppm	ppm
dcb1	2.3120	100/0	900	2850	~12000	~10000	51	~6000	285	77	185
dcb2	2.3499	100/0	500	3020	ND	ND	ND	ND	ND	ND	ND
dcb3	2.2999	100/0	900	2890	~17500	7702	32	~6000	217	58	202
dcb4	2.2825	50/0	900	3060	~38000	~7500	ND	>10000	~430	186	217
dcb5	2.2476	50/0	900	3230	39432	~7500	ND	>10000	~400	163	187
dcb6	2.3666	50/0	500	3010	ND	ND	ND	ND	ND	ND	ND
dcb7	2.2764	50/50	900	2970	~23500	~9500	27	~8000	~380	92	121
dcb8	2.2531	50/50	900	3040	~22500	~8800	26	~7500	~370	113	126
dcb9	2.2366	0/100	900	2950	5	33	ND	2147	237	ND	ND
dcb0	2.2192	0/100	900	3000	7	38	ND	2165	234	ND	ND

ND: Not detected

Table 7. Dichlobenil combustion gas yields.

Exp.	CO_2 g/g	CO g/g	$COCl_2$ g/g	HCl g/g	HCN g/g	NO g/g	N_2O g/g
dcb1	~0.739	~0.392	0.007	~0.306	0.011	0.003	0.011
dcb2	ND	ND	ND	ND	ND	ND	ND
dcb3	~1.099	0.308	0.004	~0.312	0.008	0.002	0.013
dcb4	~1.273	~0.160	ND	>0.278	~0.009	0.004	0.007
dcb5	1.416	~0.171	ND	>0.297	~0.009	0.004	0.007
dcb6	ND	ND	ND	ND	ND	ND	ND
dcb7	~1.532	~0.394	0.004	~0.432	~0.015	0.004	0.008
dcb8	~1.517	~0.378	0.004	~0.419	~0.015	0.005	0.009
dcb9	0.000	0.001	ND	0.117	0.010	ND	ND
dcb0	0.000	0.002	ND	0.121	0.010	ND	ND
Theoretical max.	1.791	-	-	0.424	-	0.174	-

ND: Not detected

Table 8. Glyphosate (isopropylamine salt) combustion gas concentrations.

Exp.	Amount	Flow	Temp.	Time	CO_2	CO	HCN	NO	N_2O	NH_3*
	g	l/h	°C	sec.	ppm	ppm	ppm	ppm	ppm	ppm
gly1	3.3020	100	900	3030	16438	54	148	ND	512	ND
gly2	3.2854	100	500	3170	~200	676	ND	ND	ND	~2000

ND: Not detected
*: Estimate based on a single reference spectrum

Table 9. Glyphosate (isopropylamine salt) combustion gas yields.

Exp.	CO_2	CO	HCN	NO	N_2O	NH_3*
	g/g	g/g	g/g	g/g	g/g	g/g
gly1	0.754	0.002	0.004	ND	0.023	ND
gly2	~0.010	0.021	ND	ND	ND	~0.037
Theoretical max.	0.717	-	-	0.163	-	-

ND: Not detected
*: Estimate based on a single reference spectrum

Table 10. Thiram combustion gas concentrations.

Exp.	Amount	Flow	Temp.	Time	CO_2	CO	HCN	SO_2	NO	N_2O	CS_2*	COS*
	g	l/h	°C	sec.	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
thl1	1.3256	100	900	2730	9338	157	100	~5500	~260	134	ND	ND
thi2	1.2739	100	500	2930	~400	<2000	303	3111	ND	ND	~700	~700

ND: Not detected
*: Estimates based on a single reference spectrum for each compound

Table 11. Thiram combustion gas yields.

Exp.	CO2	CO	HCN	SO_2	NO	N_2O	CS_2*	COS*
	g/g	g/g	g/g	g/g	g/g	g/g	g/g	g/g
thi1	0.961	0.010	0.006	~0.824	~0.018	0.014	ND	ND
thi2	~0.046	<0.146	0.021	0.521	ND	ND	~0.136	~0.107
Theoretical max.	1.098	-	-	1.065	0.250	-	-	-

ND: Not detected
*: Estimates based on a single reference spectrum for each compound

Table 12. Atrazine combustion gas concentrations.

Exp.	Amount	Flow	Temp.	Time	CO_2	CO	$COCl_2$	HCl	HCN	NO	N_2O
	g	l/h	°C	sec.	ppm	ppm	ppm	ppm	ppm	ppm	ppm
atr1	2.1129	100	900	2750	24421	143	ND	3630	102	ND	628
atr2	2.0259	100	500	2990	~500	<1000	ND	ND	>800	ND	ND
atr3	1.9633	100	900	2880	38722	1640	ND	3301	~700	ND	617
atr4	0.8916	100	900	1800	~25000	2519	ND	2071	~700	ND	428

ND: Not detected

Table 13. Atrazine combustion gas yields.

Exp.	CO_2	CO	$COCl_2$	HCl	HCN	NO	N_2O
	g/g	g/g	g/g	g/g	g/g	g/g	g/g
atr1	1.588	0.006	ND	0.196	0.004	ND	0.041
atr2	~0.037	<0.047	ND	ND	>0.036	ND	ND
atr3	2.838	0.077	ND	0.200	~0.032	ND	0.045
atr4	~2.522	0.162	ND	0.173	~0.043	ND	0.043
Theoretical max.	1.632	-	-	0.169	-	0.695	

ND: Not detected

Table 14. Dimethoate combustion gas concentrations.

Exp.	Amount	Flow	Temp.	Time	CO_2	CO	HCN	SO_2	NO	N_2O	CH_4*	COS*
	g	l/h	°C	sec.	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
dim1 (pure compound)	2.5201	100	900	3000	14520	1455	245	~5000	ND	232	~500	~100
dim2 (formulation)	2.8717	100	900	3030	35795	179	ND	2613	ND	134	ND	ND

ND: Not detected
*: Estimates based on a single reference spectrum for each compound

Table 15. Dimethoate combustion gas yields.

Exp.	CO_2	CO	HCN	SO_2	NO	N_2O	CH_4*	COS*
	g/g	g/g	g/g	g/g	g/g	g/g	g/g	g/g
dim1 (pure compound)	0.864	0.055	0.009	~0.433	ND	0.014	~0.011	~0.008
dim2 (formulation)	1.887	0.006	ND	0.201	ND	0.007	ND	ND
Theoretical max. (pure)	0.960	-	-	0.558	0.131	-	-	-

ND: Not detected
*: Estimates based on a single reference spectrum for each compound

4.4 Identification of organic decomposition products

Off-line GC/MS analyses of organic products were part of previous DIN experiments in which lindane and dimethoate (among others) were examined (Smith-Hansen & Jørgensen, 1992). This type of analyses have not been carried out in the experiments reported here. However, it has been possible to identify a number of organic products on basis of the FTIR spectra. In some of the 500 °C experiments organic products were present in substantial amounts. At 900 °C only small amounts of organic products were seen in two of the experiments.

Lindane:	No signs of organic products in the spectra.
Dichlobenil:	At 500 °C a mixture of 2,6-dichlorobenzonitrile (dichlobenil) and 2,6-dichlorotoluene was seen in the beginning. After a few minutes only 2,6-dichlorotoluene could be seen.
	At 900 °C with N_2 a mixture of 2,6-dichlorobenzonitrile (dichlobenil) and 1,3-dichlorobenzene was seen in the beginning. After a few minutes only 1,3-dichlorobenzene could be seen.
Glyphosate:	At 500 °C isopropylamine dominated the spectra.
Thiram:	At 500 °C N,N-dimethylformamide was a major product.
Atrazine:	At 500 °C propene and a compound which probably was an isocyanate dominated the spectra.
Dimethoate:	At 900 °C CH_4 was detected from the pure substance but not from the formulation.

4.5 Discussion

Lindane

With a sample of 3 g the CO_2 production was significantly higher than with a sample of 1 or 2 g. This resulted in a CO_2/CO ratio of 0.5 while it was 0.2 in the other experiments. The production of HCl increased slightly with a decreasing sample load but it was between 70 and 80% of the theoretical value in all experiments. These findings are in agreement with previous DIN experiments (Smith-Hansen & Jørgensen, 1992). The highest production of $COCl_2$ was seen with a sample of 1 g - about 200% of the production with a sample of 2 or 3 g.

Dichlobenil

In these experiments the residence time or the oxygen concentration seemed to have an effect on the production of some compounds but not on others. A CO_2/CO ratio of around 2.5 was seen in the experiments with a flow of 100 l/h of air or air/N_2 mixture while the ratio was about twice as large in the experiments with reduced flow. The flow (residence time) also seemed to influence the $COCl_2$ production: At 900 °C the production was at the same level in 100 l/h experiments with normal and reduced oxygen concentration while no $COCl_2$ could be detected in the 50 l/h experiments. The HCl production on the other hand, was highest with the air/N_2 mixture (100% of the theoretical value) and somewhat lower with pure air (~70% of the theoretical value) but independent of the

airflow. The production of HCN seemed to behave in the same way but the amounts produced were much smaller. In the experiments with pure N_2 the production of HCN was at the same level as in the other experiments while the HCl production was reduced to ~30% of the theoretical value.

In the 500 °C experiments 2,6-dichlorotoluene was the only decomposition product detected and at 900 °C with pure N_2 1,3-dichlorobenzene was detected along with the other products.

Glyphosate

A very high CO_2/CO ratio (~300) was seen at 900 °C and only small amounts of CO and HCN were detected. At 500 °C very little happened; isopropylamine dominated the spectra in which also CO, NH_3 and small amounts of CO_2 were seen.

Thiram

A CO_2/CO ratio of 59 and a high production of SO_2 was seen at 900 °C but no other sulphur compounds were detected. At 500 °C, however, the production of SO_2 was lower and CS_2 and COS were found in significant amounts.

Atrazine

At 900 °C the production of HCl and CO_2 were found to be higher than their theoretical maxima in some experiments. Comparison with calibration spectra did not reveal any errors in the predictions and the problem therefore most likely is caused by errors in the flow measurement in these experiments.

The finding of propene in the 500 °C experiment is in agreement with the degradation process (polycondensation followed by oxidation) proposed by Matuschek et al (1991).

Dimethoate

At 900 °C CO_2/CO ratios of 10 and 200 were found with the pure compound and the formulation, respectively. HCN, CH_4 and COS were only detected from the pure compound. This is not quite in agreement with previous DIN experiments in which a higher CO_2/CO ratio was found for the pure compound and no HCN was detected.

5 Conclusion

In the present work flash pyrolysis-GC/MS have been used in connection with DIN combustion experiments to investigate the thermal decomposition products from chemicals. In the flash pyrolysis-GC/MS experiments it was observed that:

- substances with only small differences in chemical structure may generate very different product mixtures when heated
- differences in the product mixtures seem to correlate reasonably with the expected stability/reactivity of the compounds subjected to pyrolysis
- there seems to be good qualitative agreement between DIN and pyrolysis experiments but in general a wider range of products have been found in the pyrolysis experiments
- the products found in the present study are in good agreement with pyrolysis products/schemes reported in the literature

The pyrolysis-GC/MS method seems to be useful for investigations of thermal decomposition products from pesticides, but obviously it can not be used alone to predict the combustion products.

In the DIN experiments the following observations were made:

- the highest $COCl_2$ production was (as expected) found from a highly chlorinated compound
- the residence time seems to influence on the CO_2/CO ratio (increased ratio at increased residence time) and on the $COCl_2$ production (no $COCl_2$ was observed at increased residence time)
- although N_2O was measured in the present experiments along with NO_x and HCN, the fate of the greater part of the nitrogen content is still not accounted for

The FTIR instrument used for gas analyses in the present experiments offer distinct advantages compared to the single-gas analyzers used in previous experiments:

- interferences can be uncovered and - to a great extent - handled
- compounds not included in the calibrations can be identified/quantified *after* the experiments

The disadvantage connected with the FTIR measurements is the significant initial effort needed for calibrations, development of quantification routines etc.

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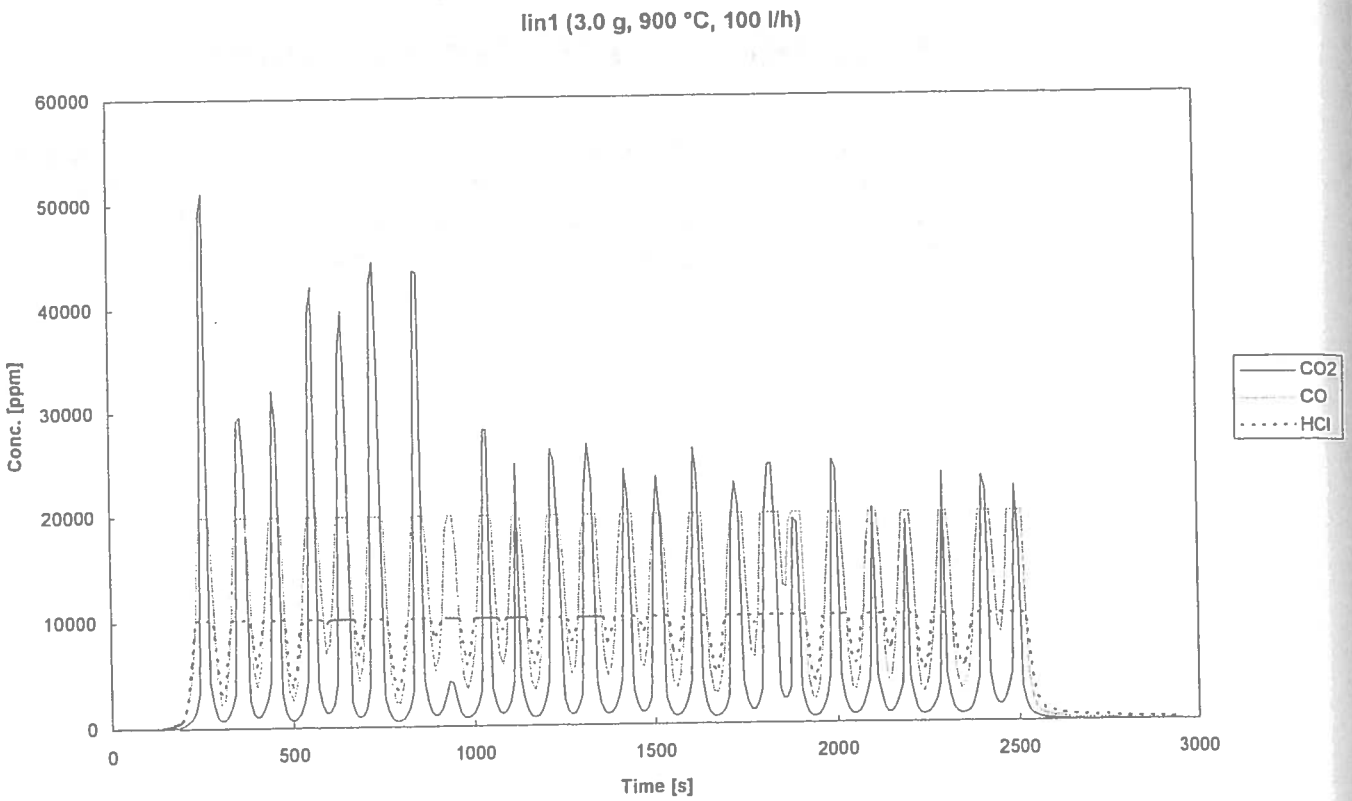
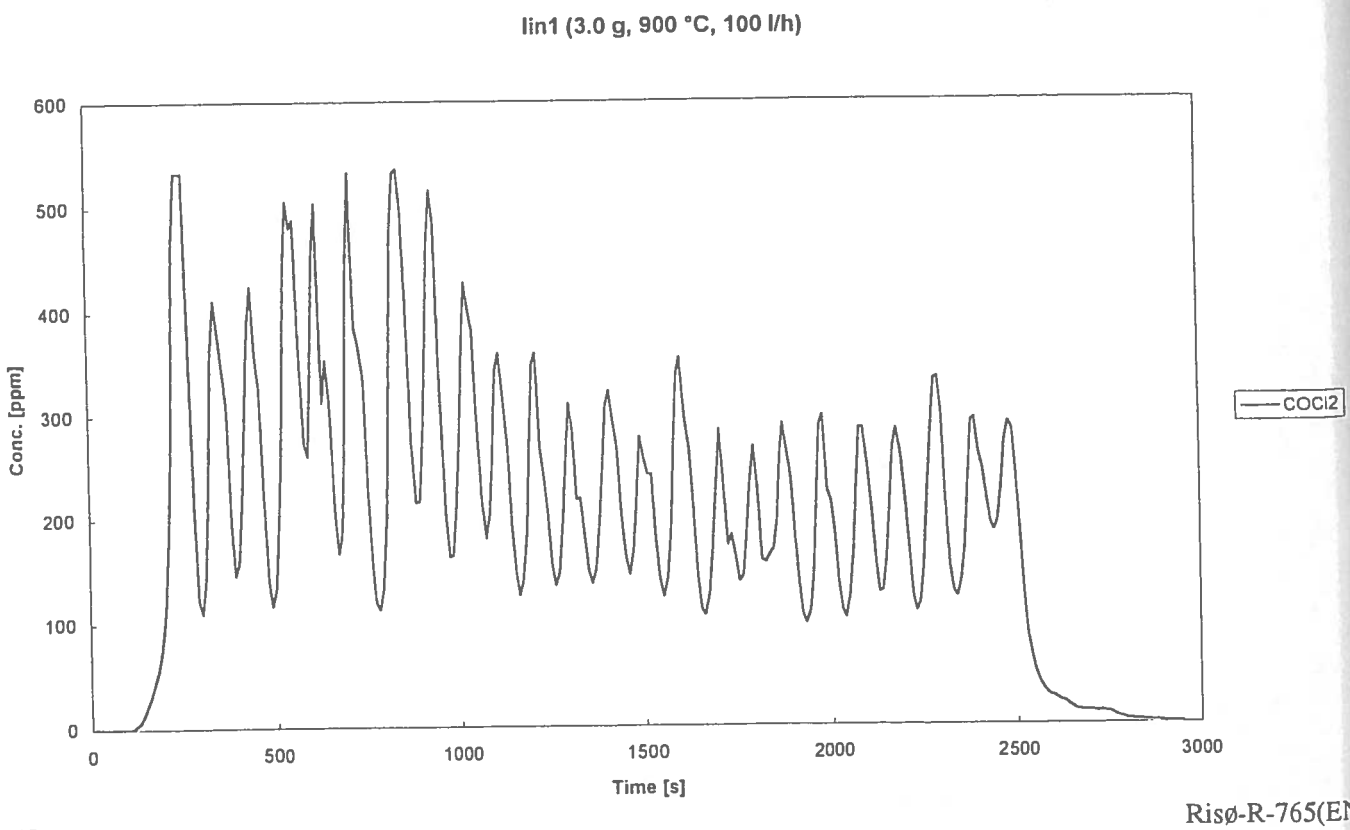
A On-line FTIR measurements

Plots showing the measured concentrations as a function of time are presented on the following pages. It should be noted that the concentrations shown are the uncorrected results from the automatic quantification. A few plots have been omitted because strong interferences made the results questionable: CO_2 from gly2; CO_2 and CO from thi2; CO_2 and CO from atr2.


lin1 (3.0 g, 900 °C, 100 l/h)
Conc. [ppm]
Time [s]
CO2
CO
HCl
0
10000
20000
30000
40000
50000
60000
0
500
1000
1500
2000
2500
3000

LIN_RES.XLS


lin1 (3.0 g, 900 °C, 100 l/h)
Conc. [ppm]
Time [s]
COCl2
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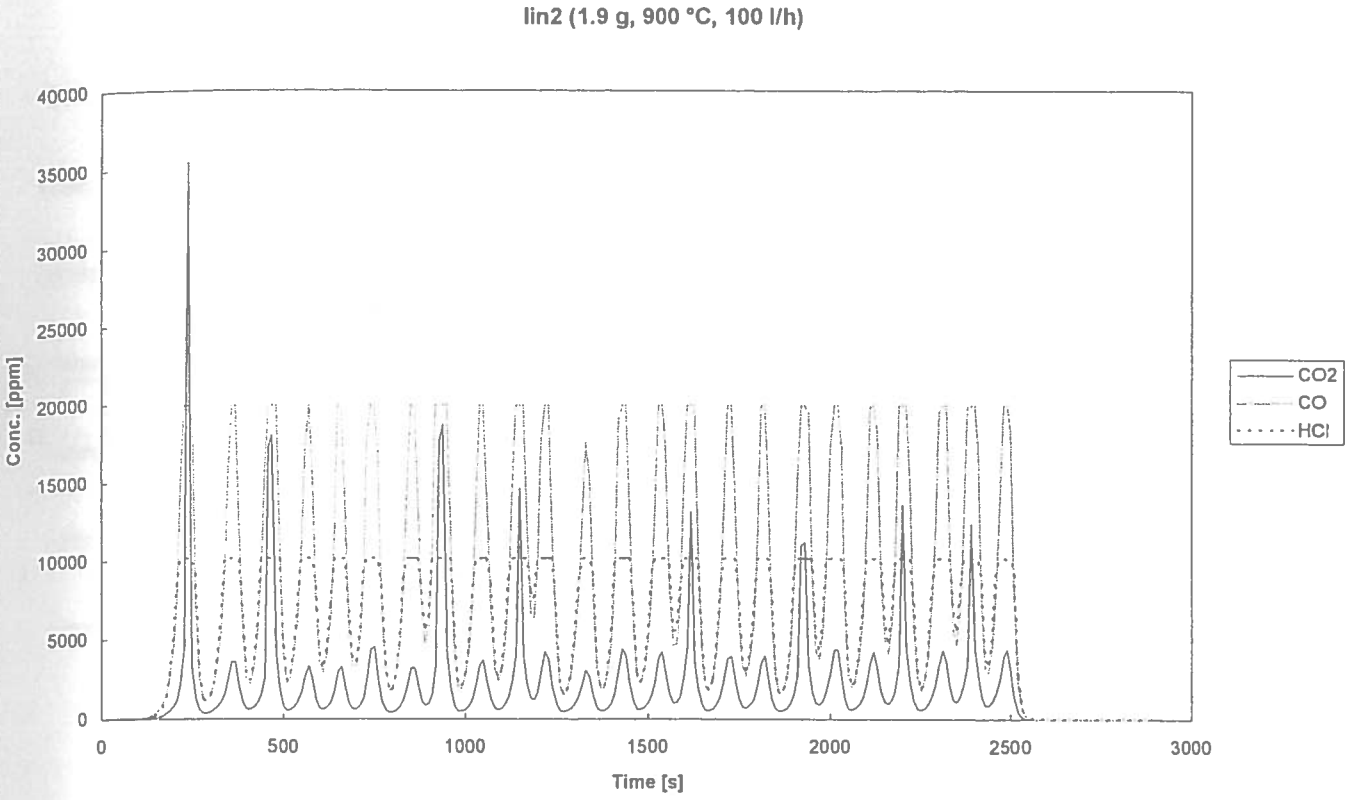
100
200
300
400
500
600
0
500
1000
1500
2000
2500
3000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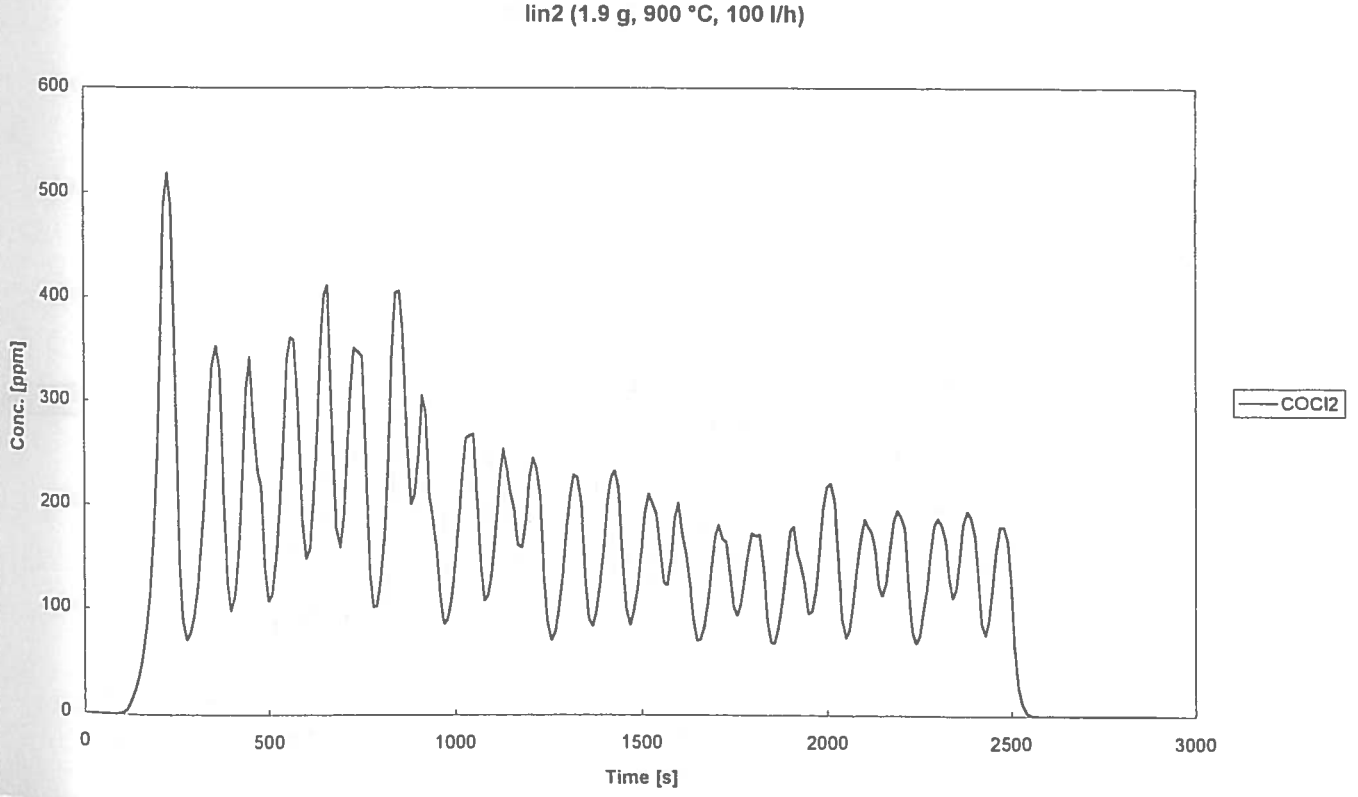
Conc. [ppm]
Time [s]
CO2
CO
HCl

LIN_RES.XLS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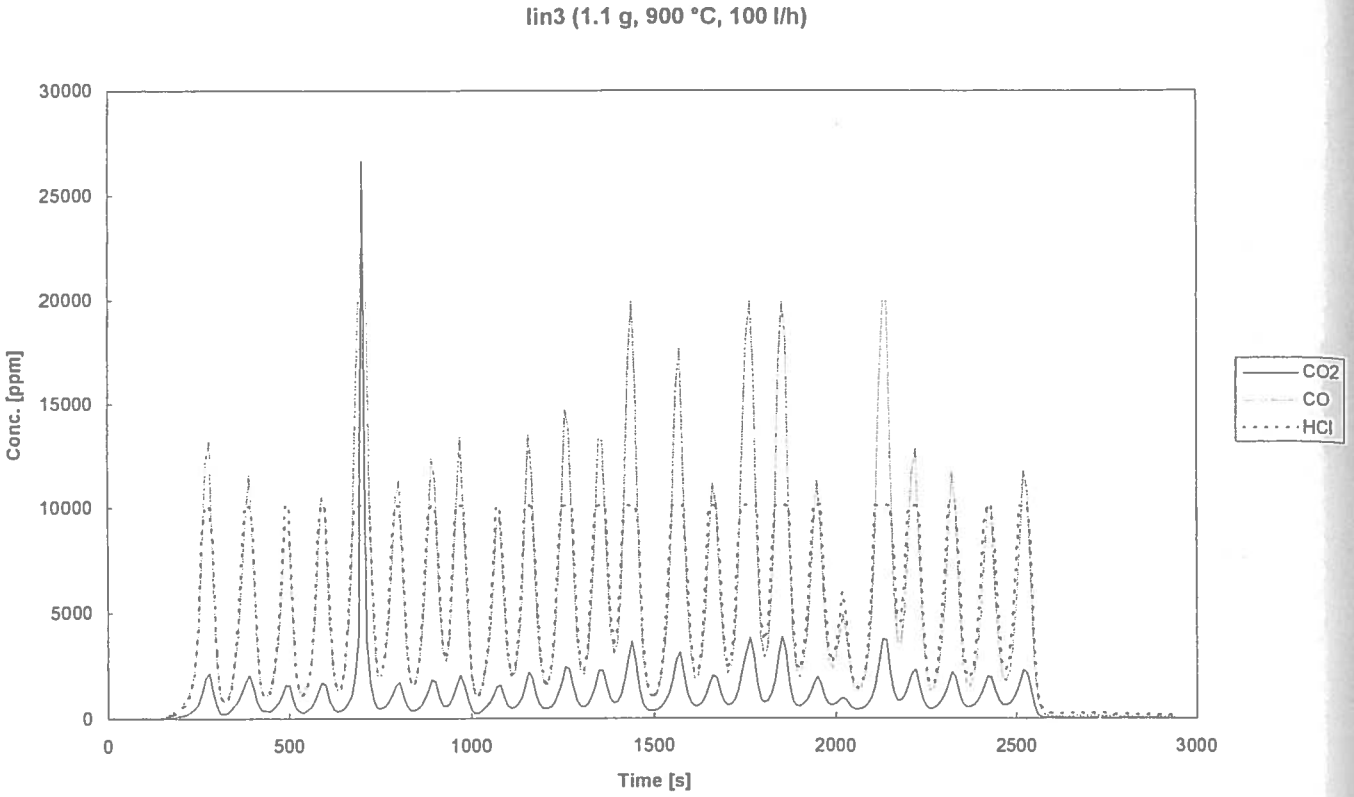
Conc. [ppm]
Time [s]
COCl2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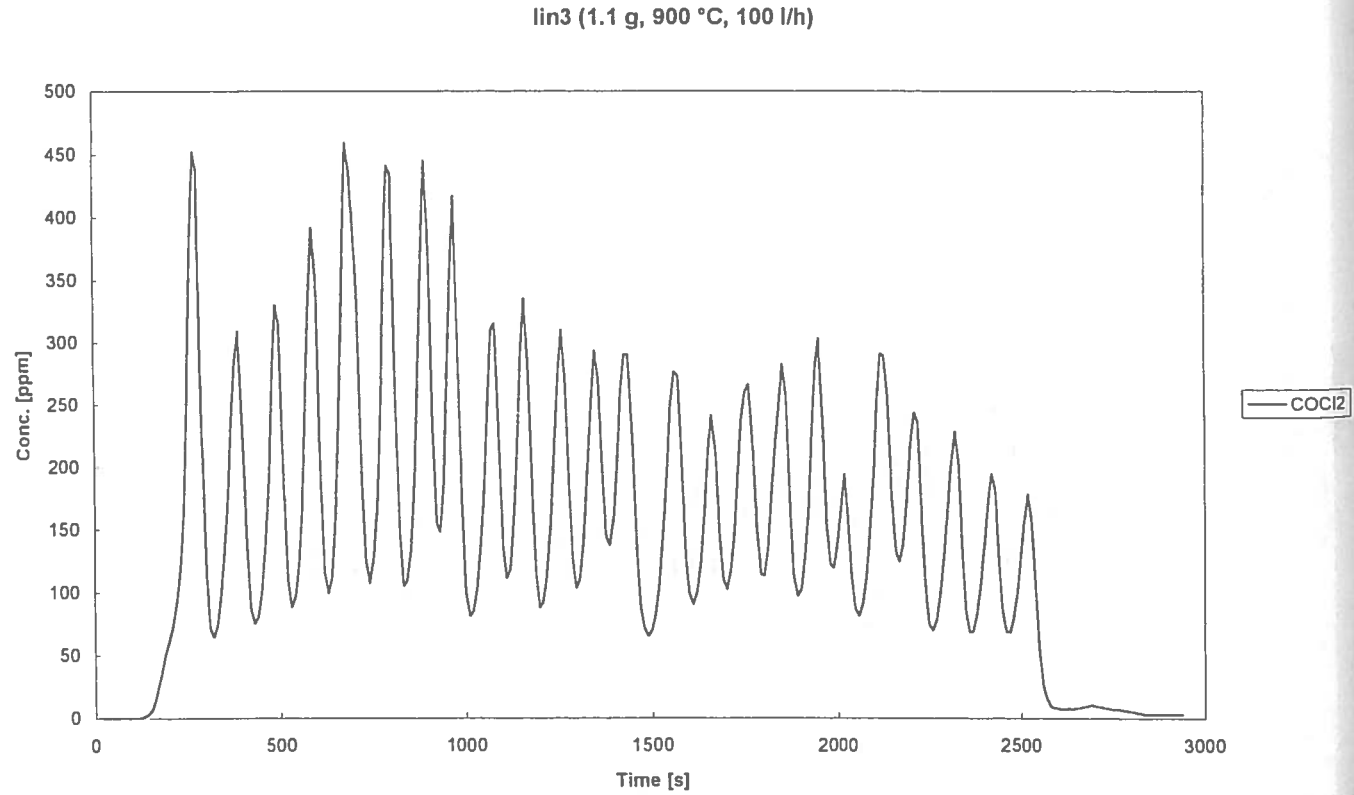
Conc. [ppm]
Time [s]
CO2
CO
HCl

LIN_RES.XLS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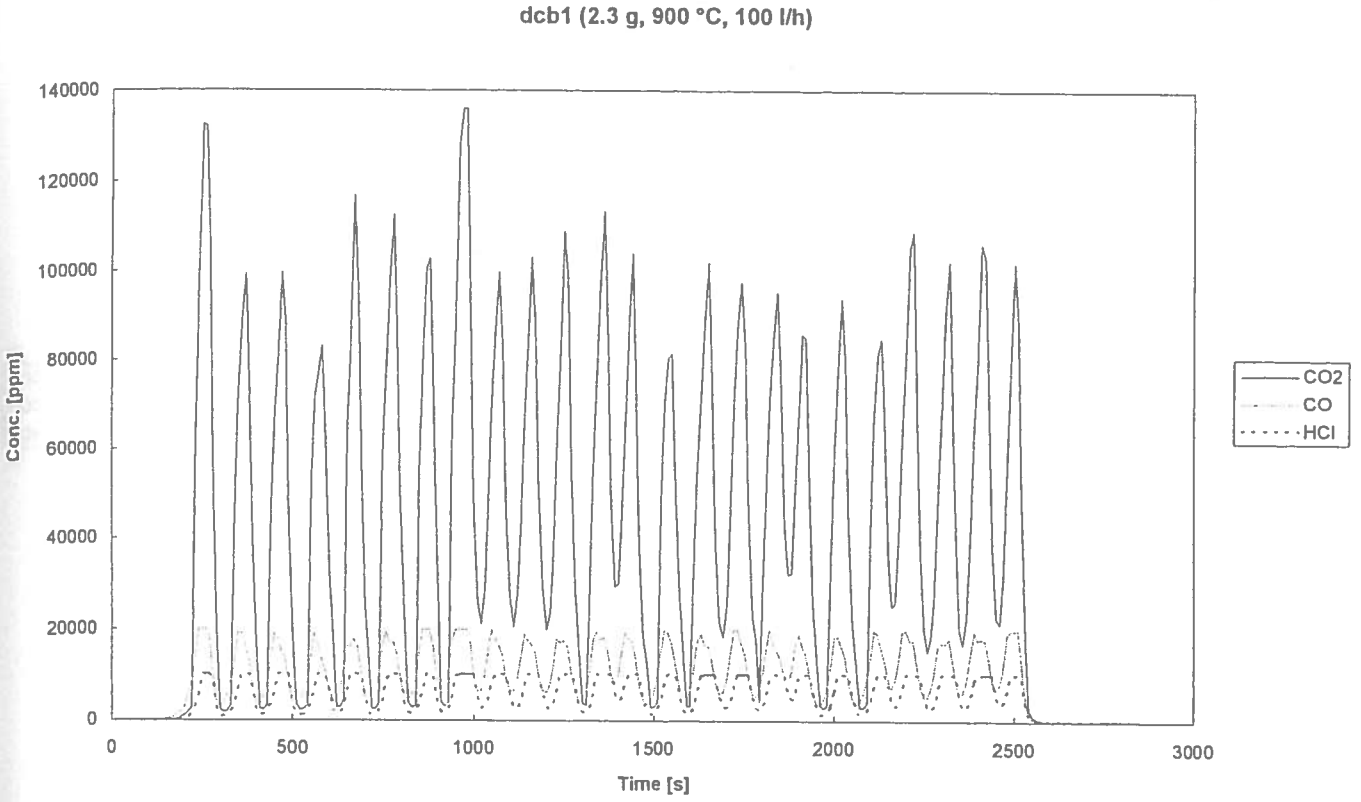
Conc. [ppm]
Time [s]
COCl2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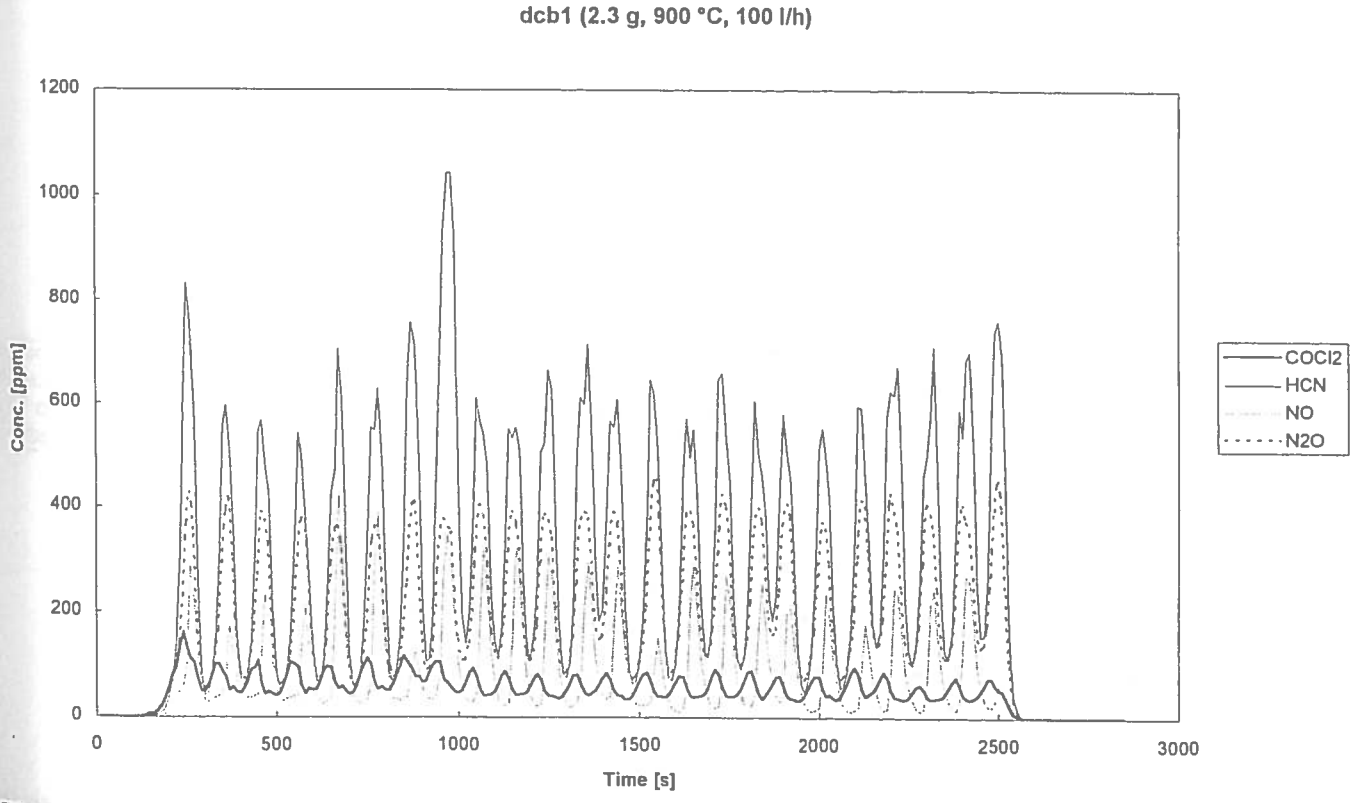
Conc. [ppm]
Time [s]
CO2
CO
HCl

DCB_RES.XLS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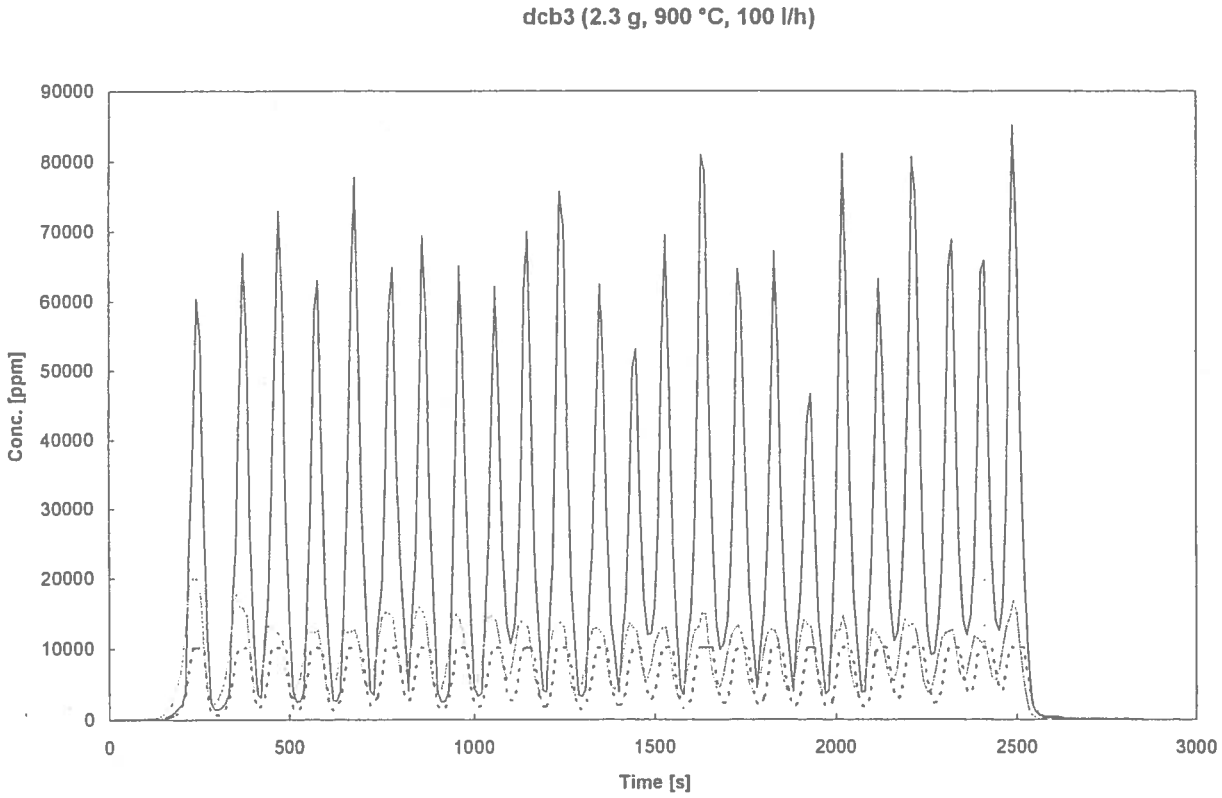
Conc. [ppm]
Time [s]
COCl2
HCN
NO
N2O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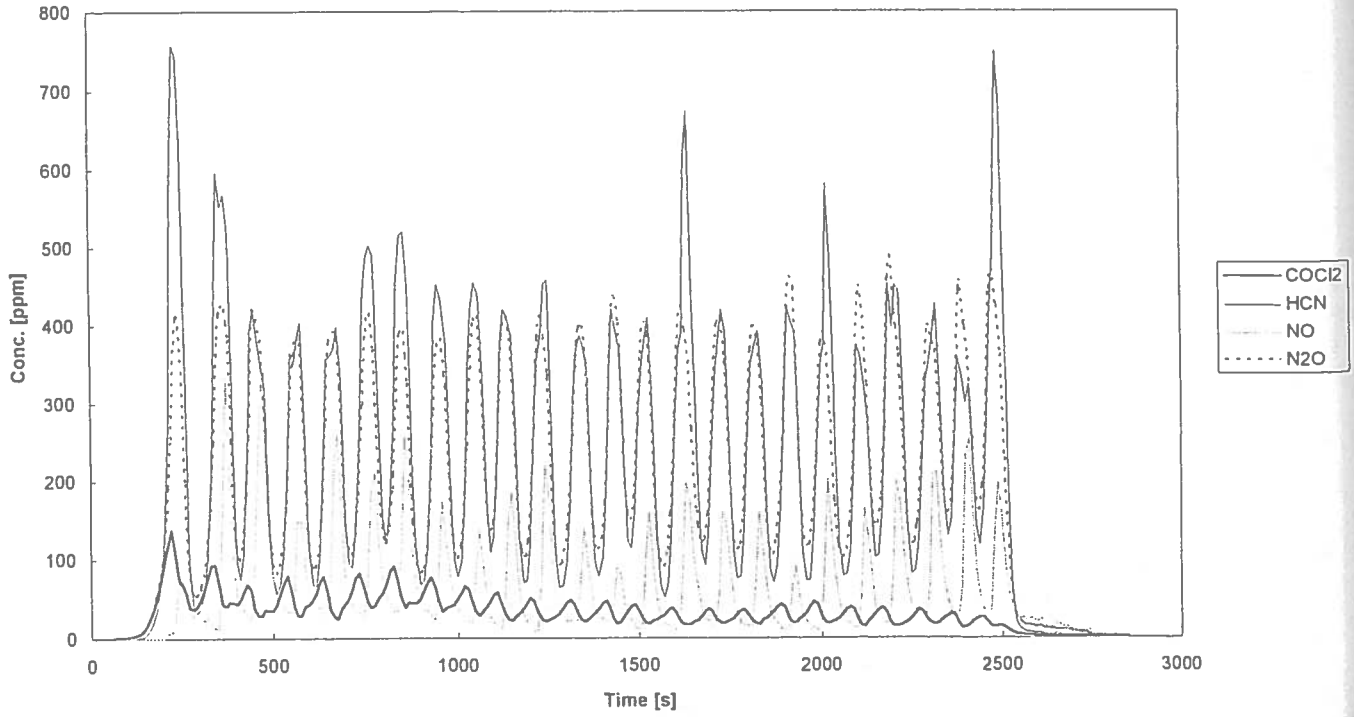
Conc. [ppm]
Time [s]
CO2
CO
HCl

DCB_RES.XLS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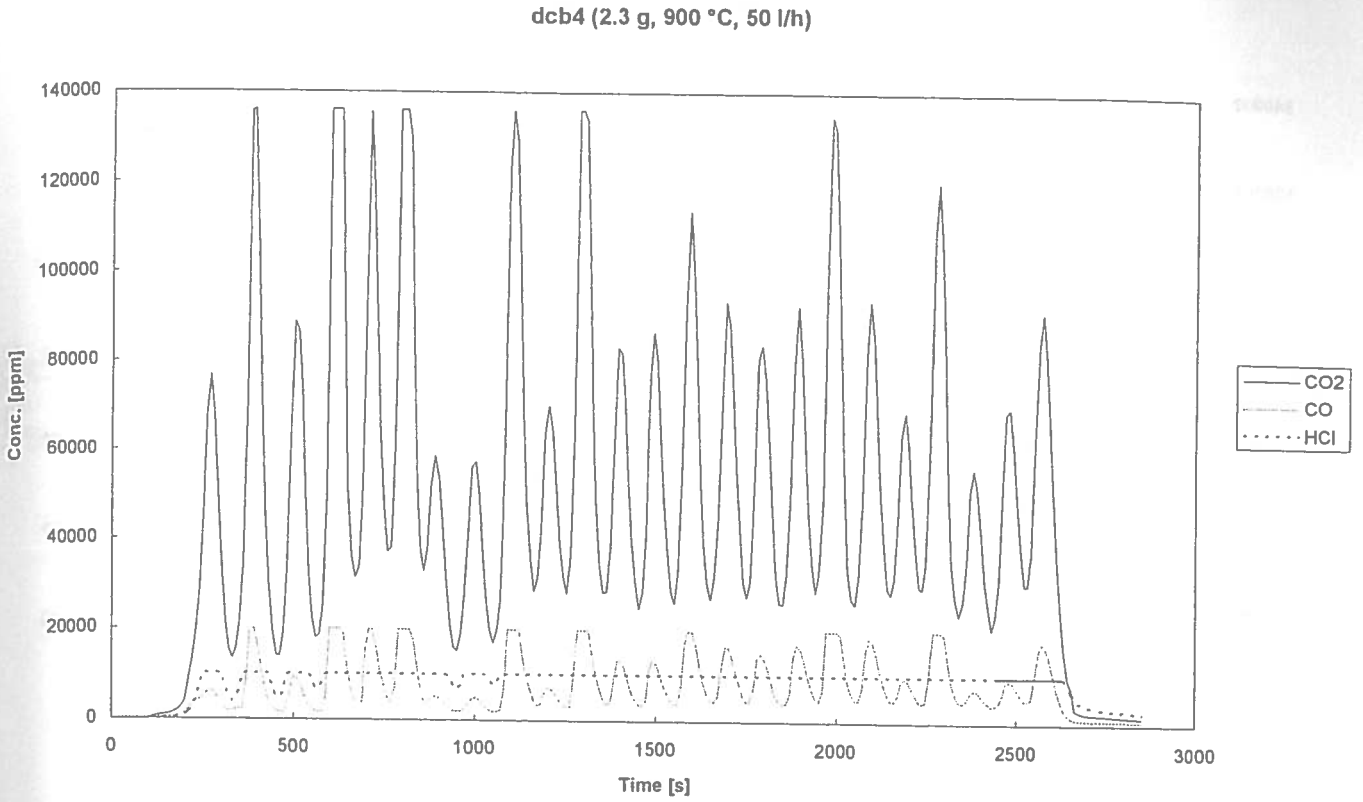
Conc. [ppm]
Time [s]
COCl2
HCN
NO
N2O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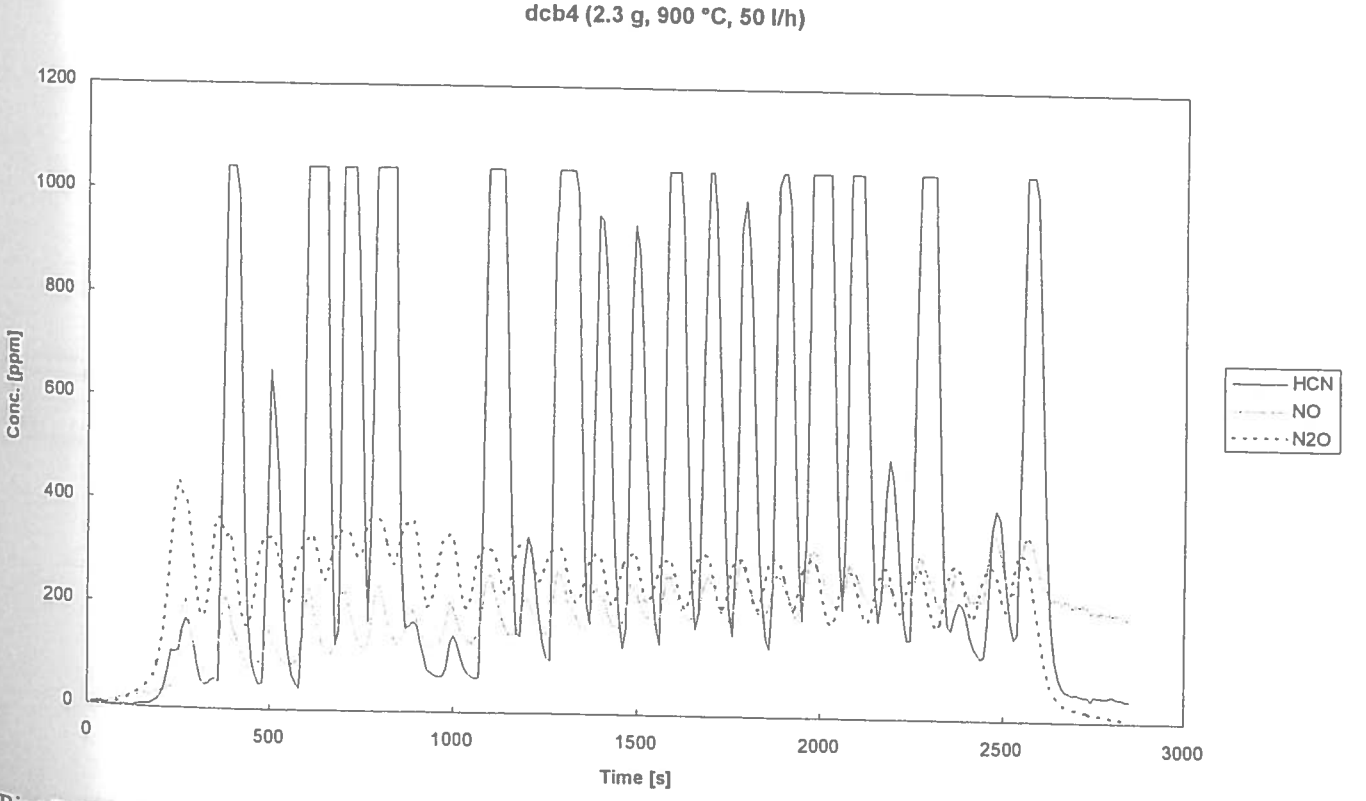
Conc. [ppm]
Time [s]
CO2
CO
HCl

DCB_RES.XLS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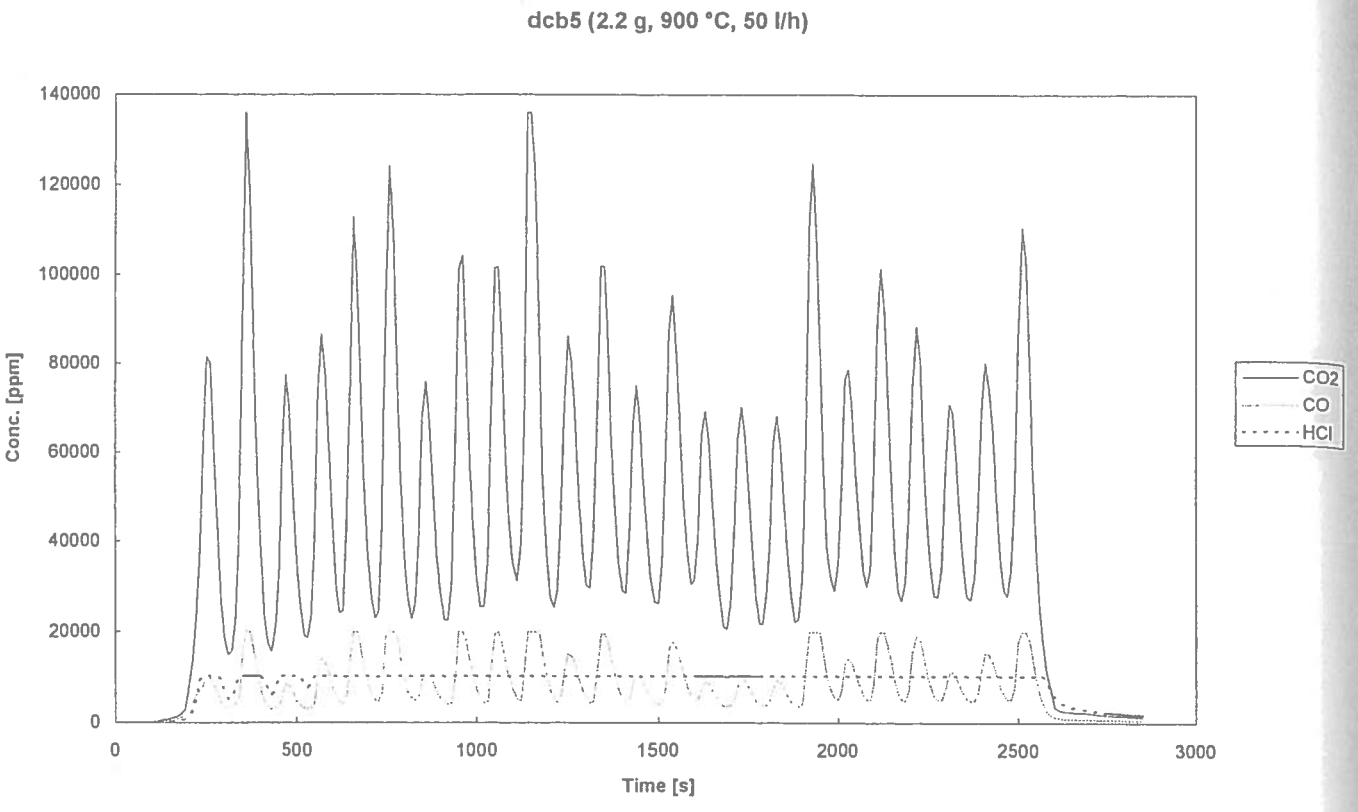
Conc. [ppm]
Time [s]
HCN
NO
N2O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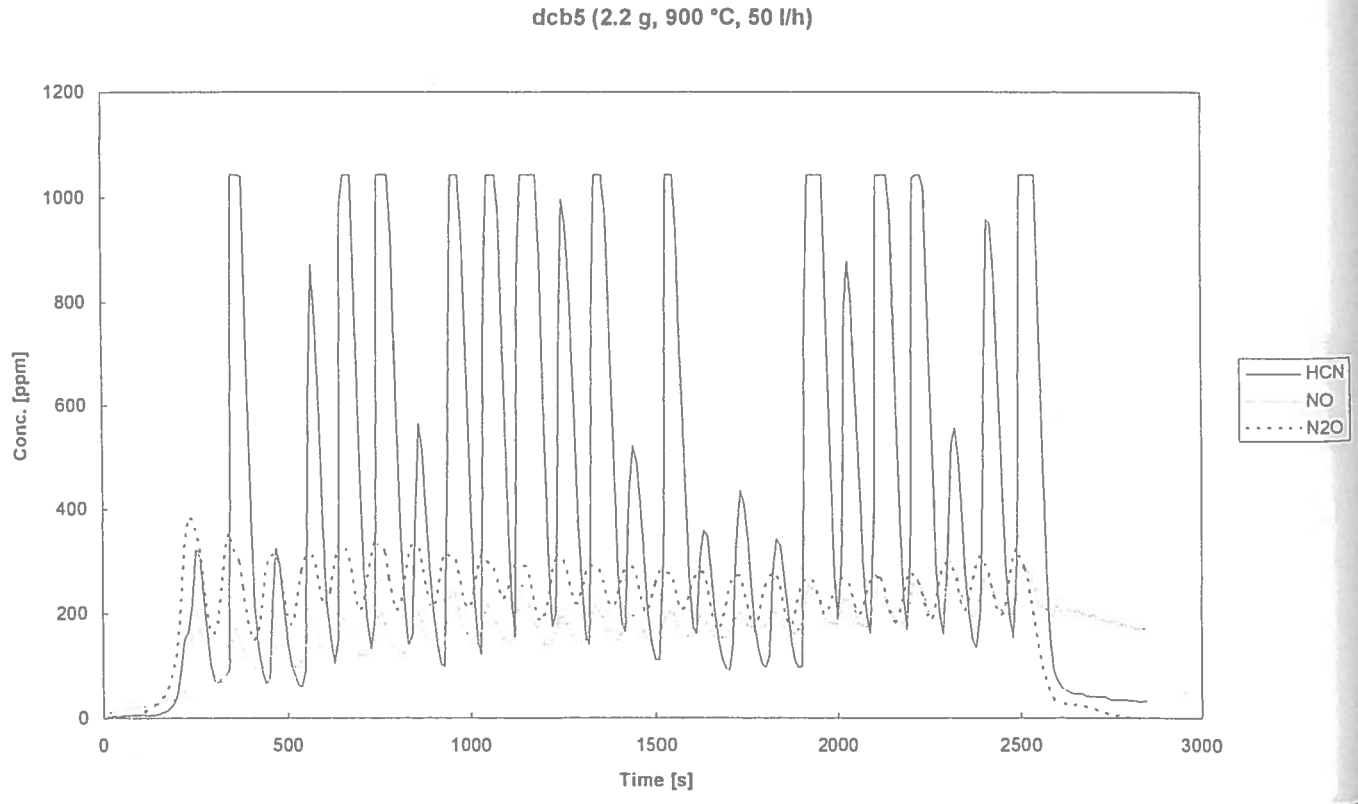
Conc. [ppm]
Time [s]
CO2
CO
HCl

DCB_RES.XLS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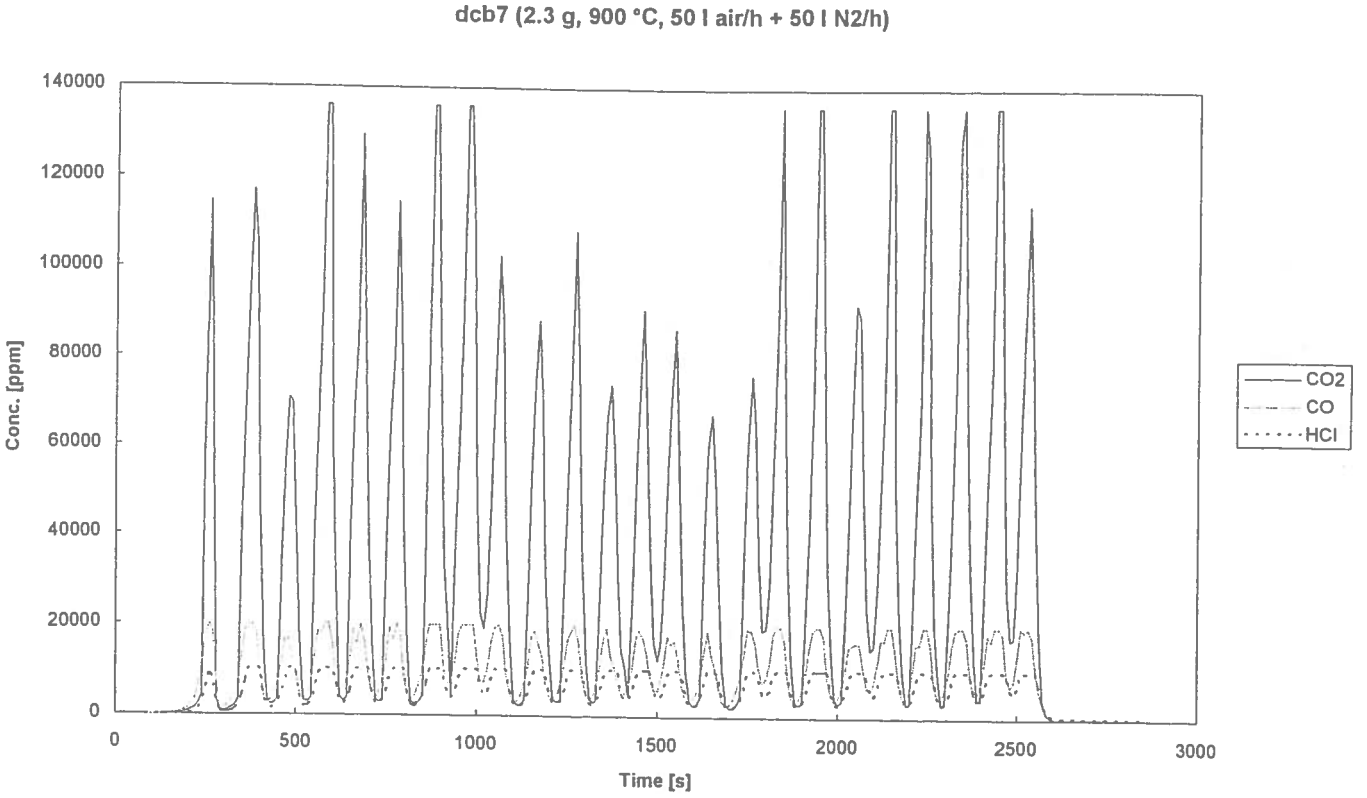
Conc. [ppm]
Time [s]
HCN
NO
N2O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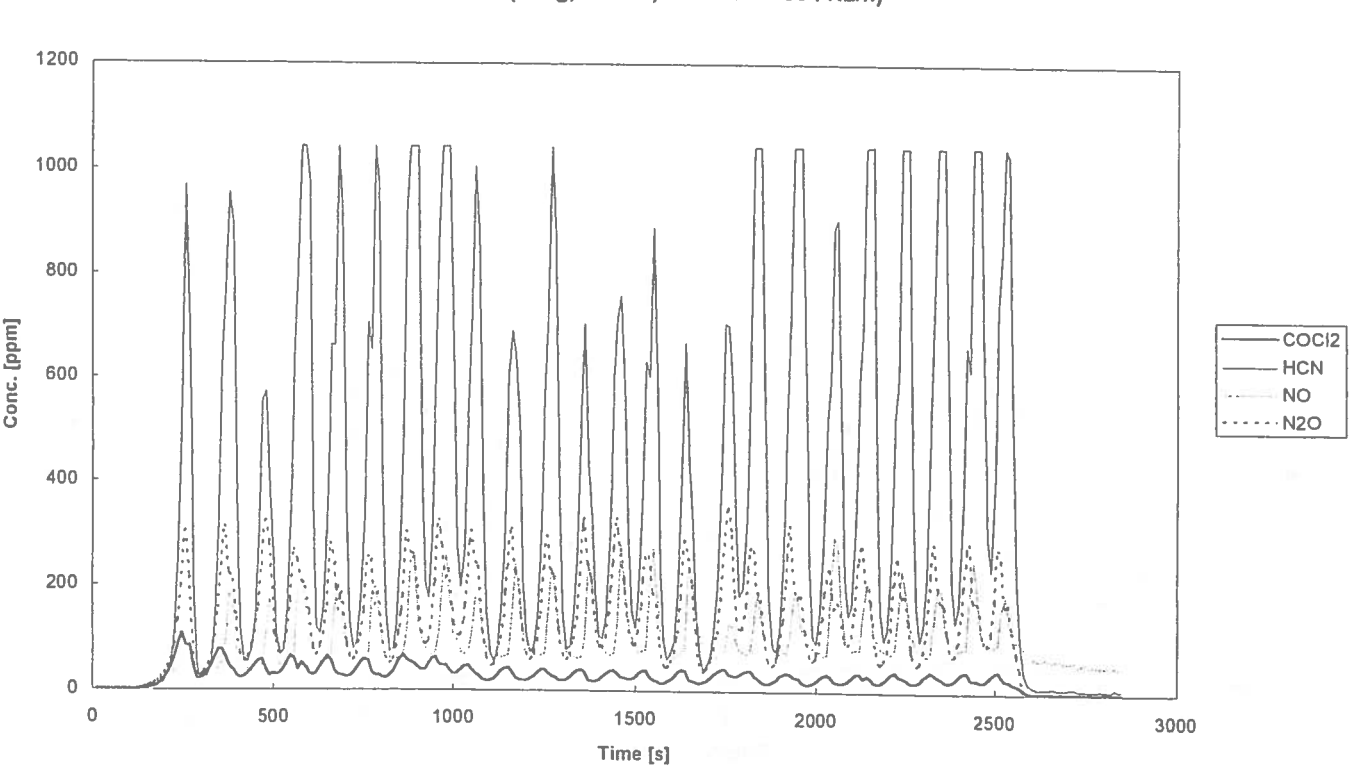
Conc. [ppm]
Time [s]
CO2
CO
HCl

DCB_RES.XLS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Conc. [ppm]
Time [s]
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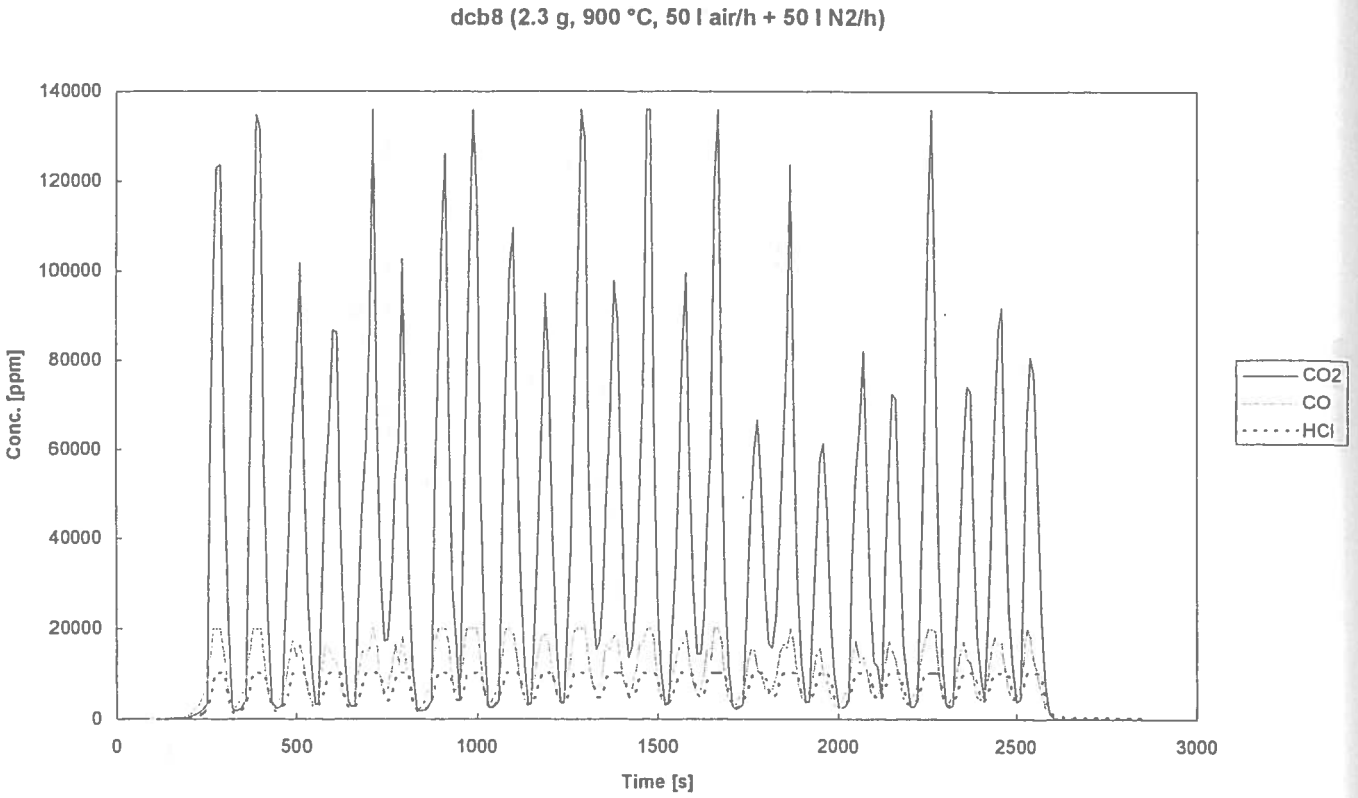
HCN
NO
N2O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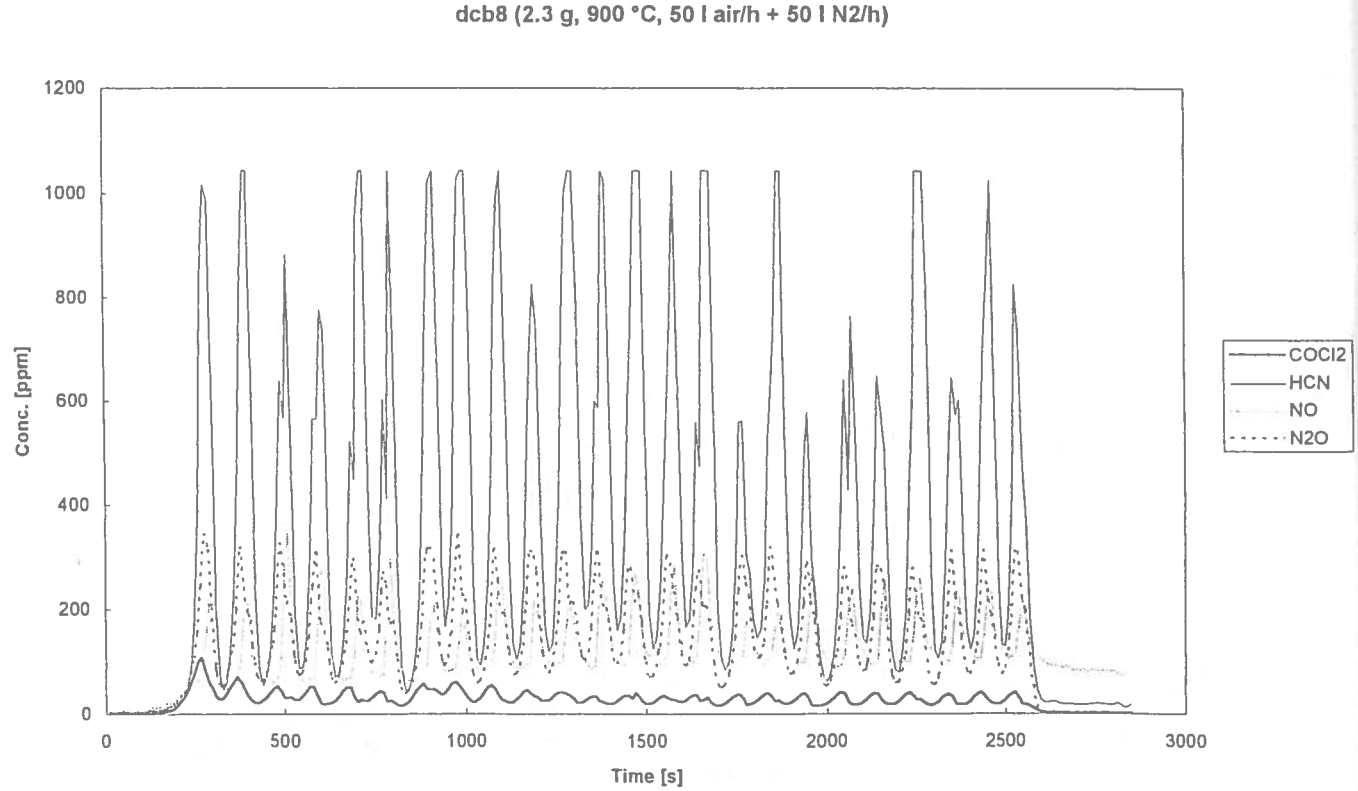
Conc. [ppm]
Time [s]
CO2
CO
HCl

DCB_RES.XLS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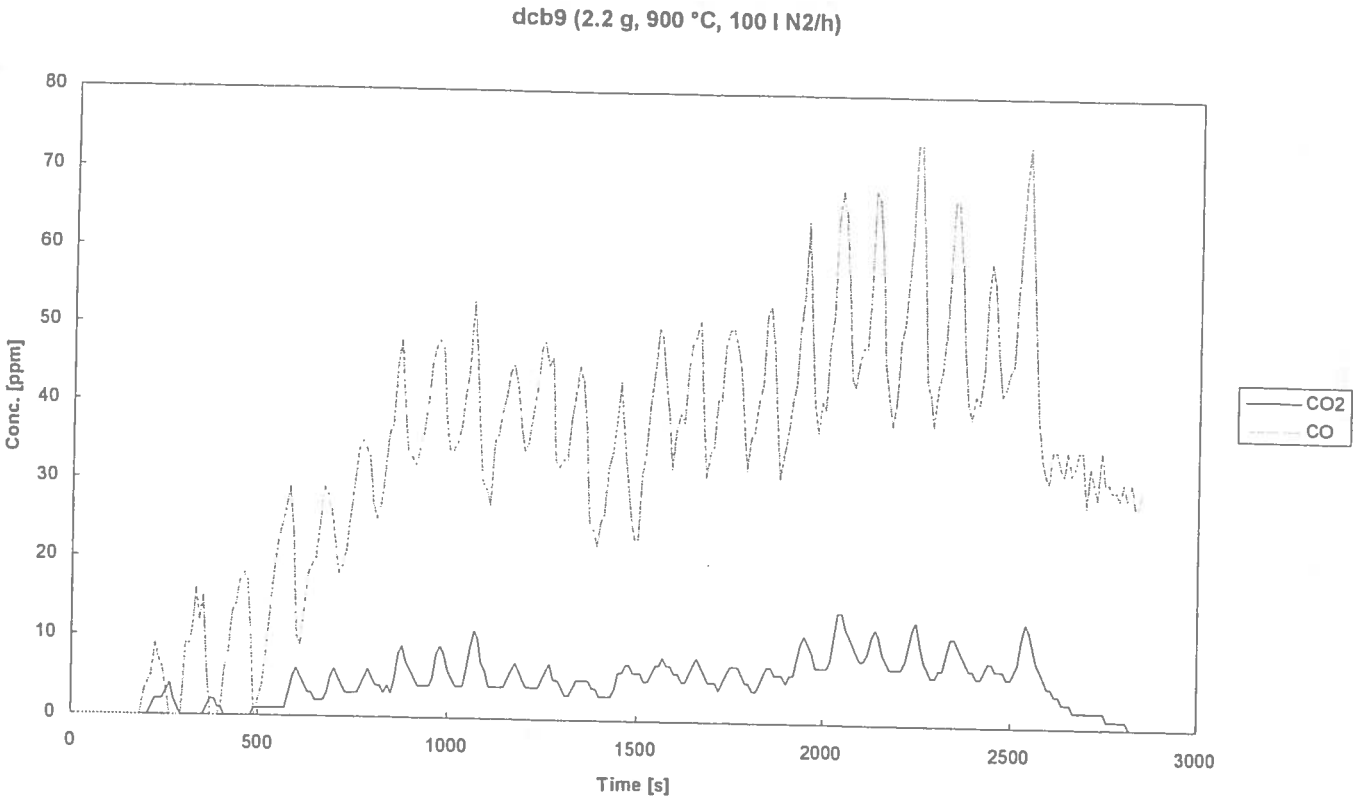
Conc. [ppm]
Time [s]
COCl2
HCN
NO
N2O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Conc. [ppm]
Time [s]
CO2
CO
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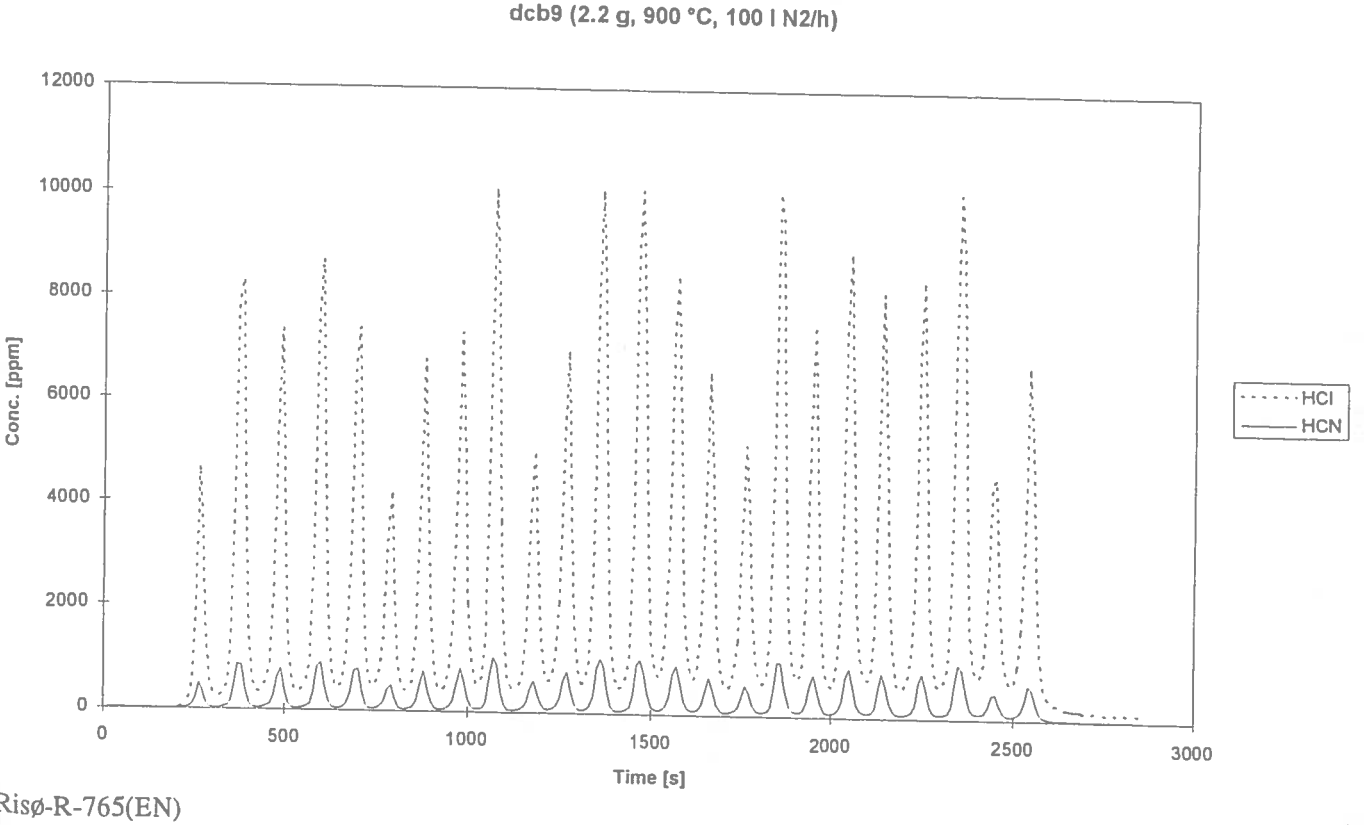
20
30
40
50
60
70
80
0
500
1000
1500
2000
2500
3000

DCB_RES.XLS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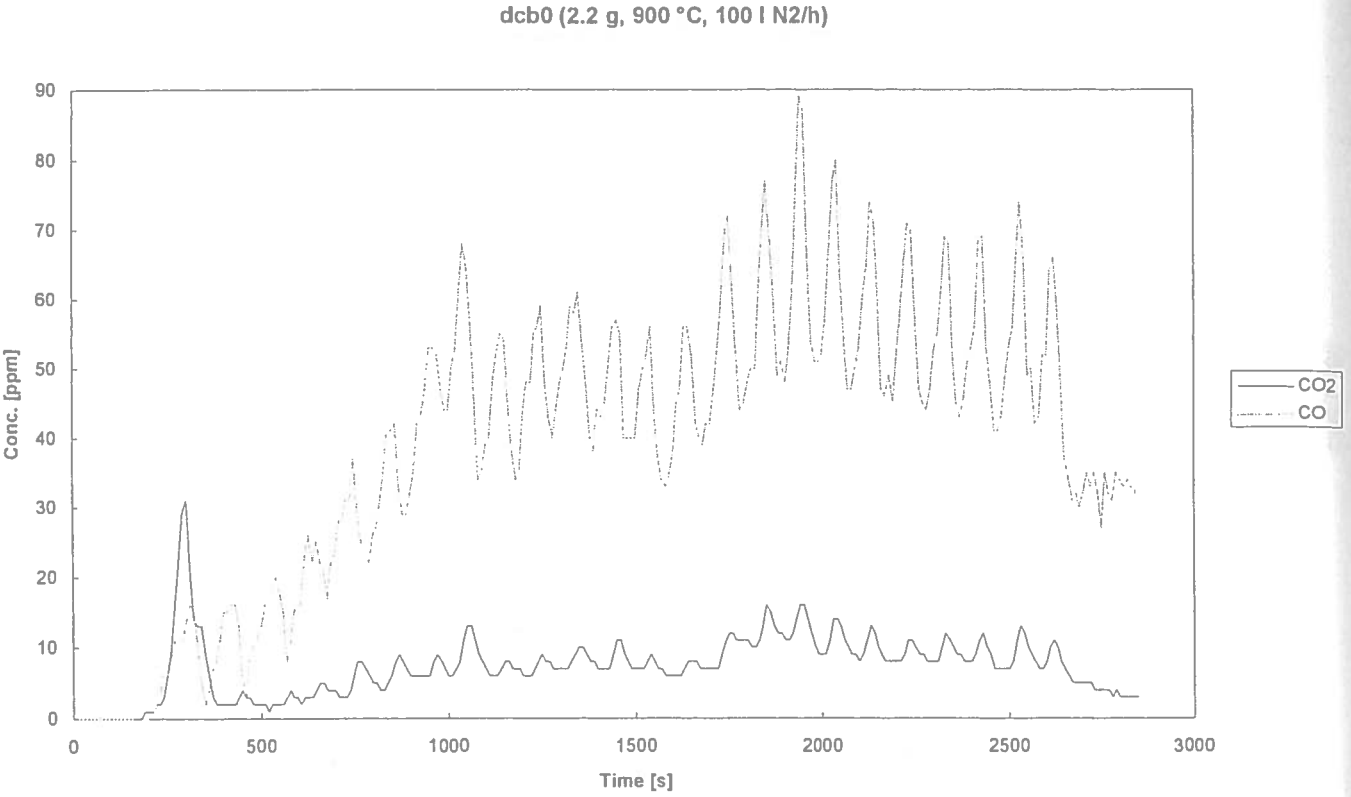
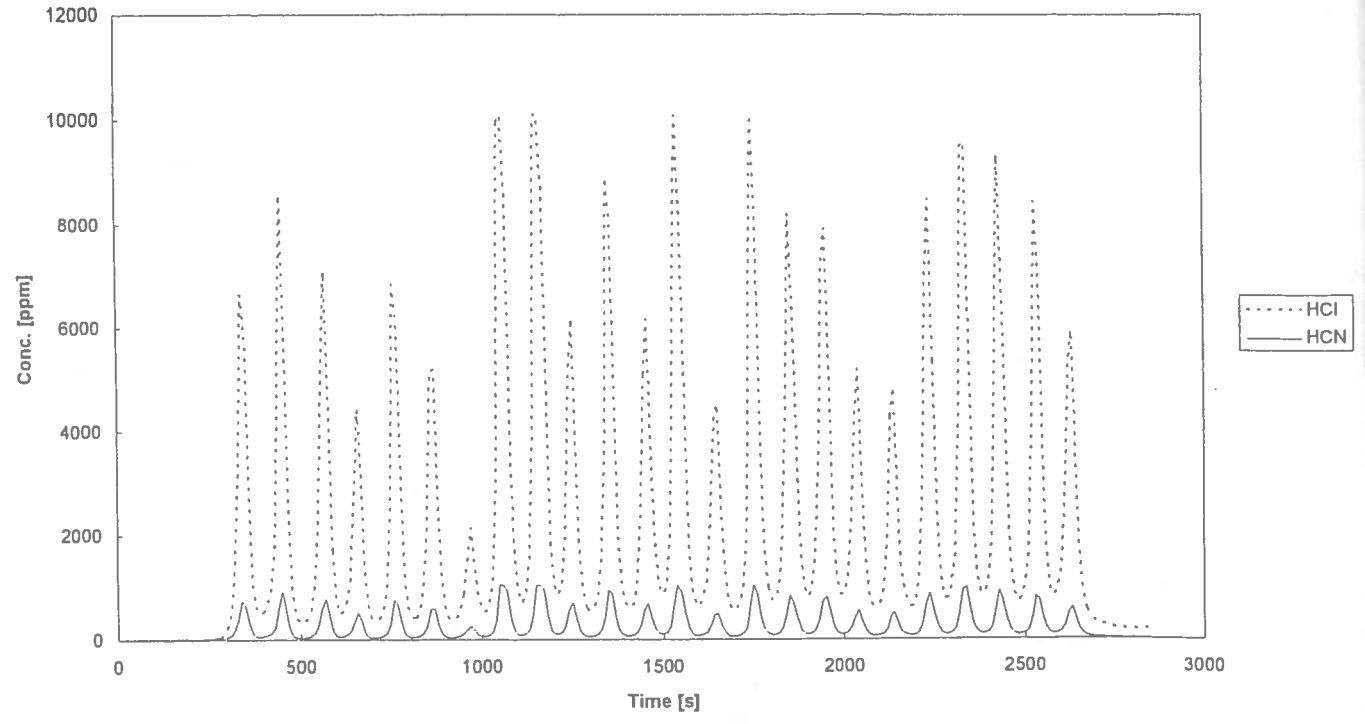
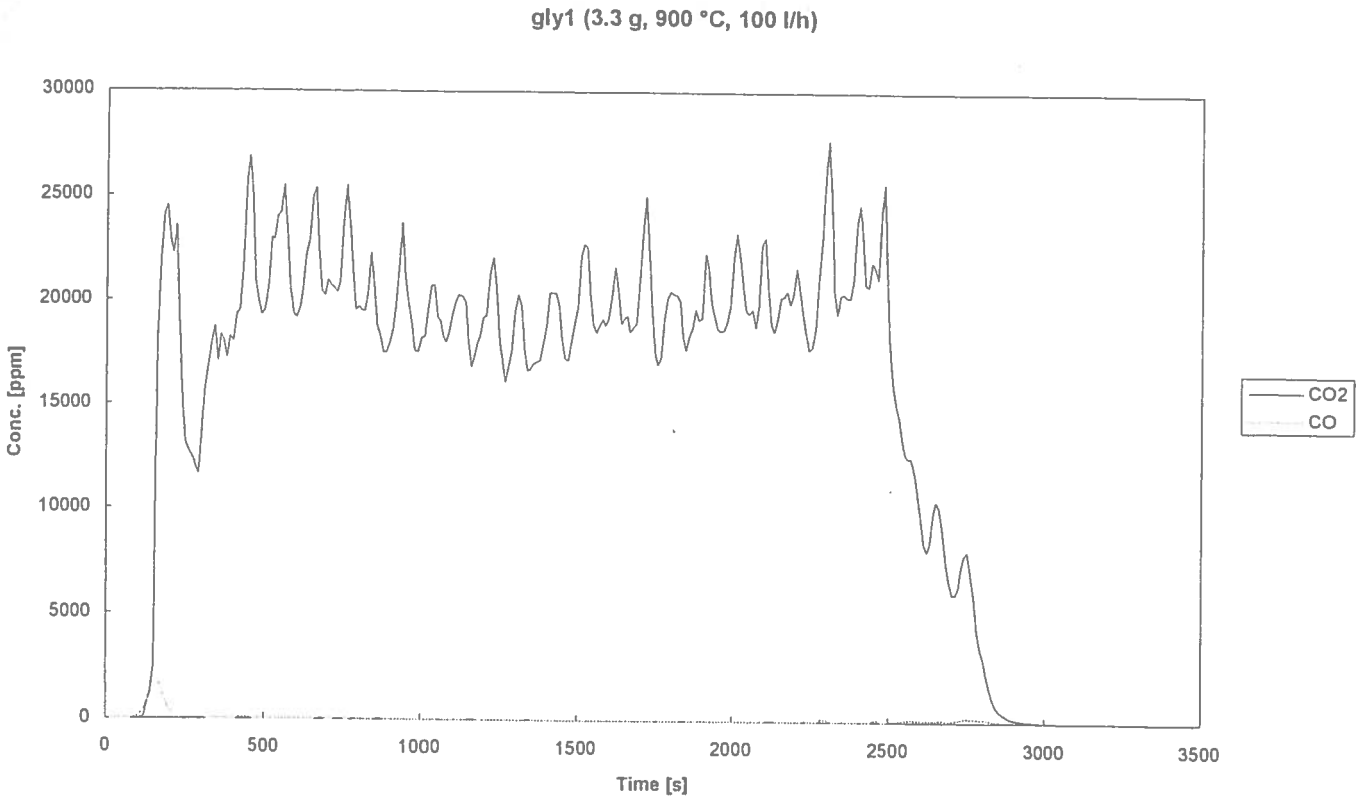
Conc. [ppm]
Time [s]
HCl
HCN
0
2000
4000
6000
8000
10000
12000
0
500
1000
1500
2000
2500
3000

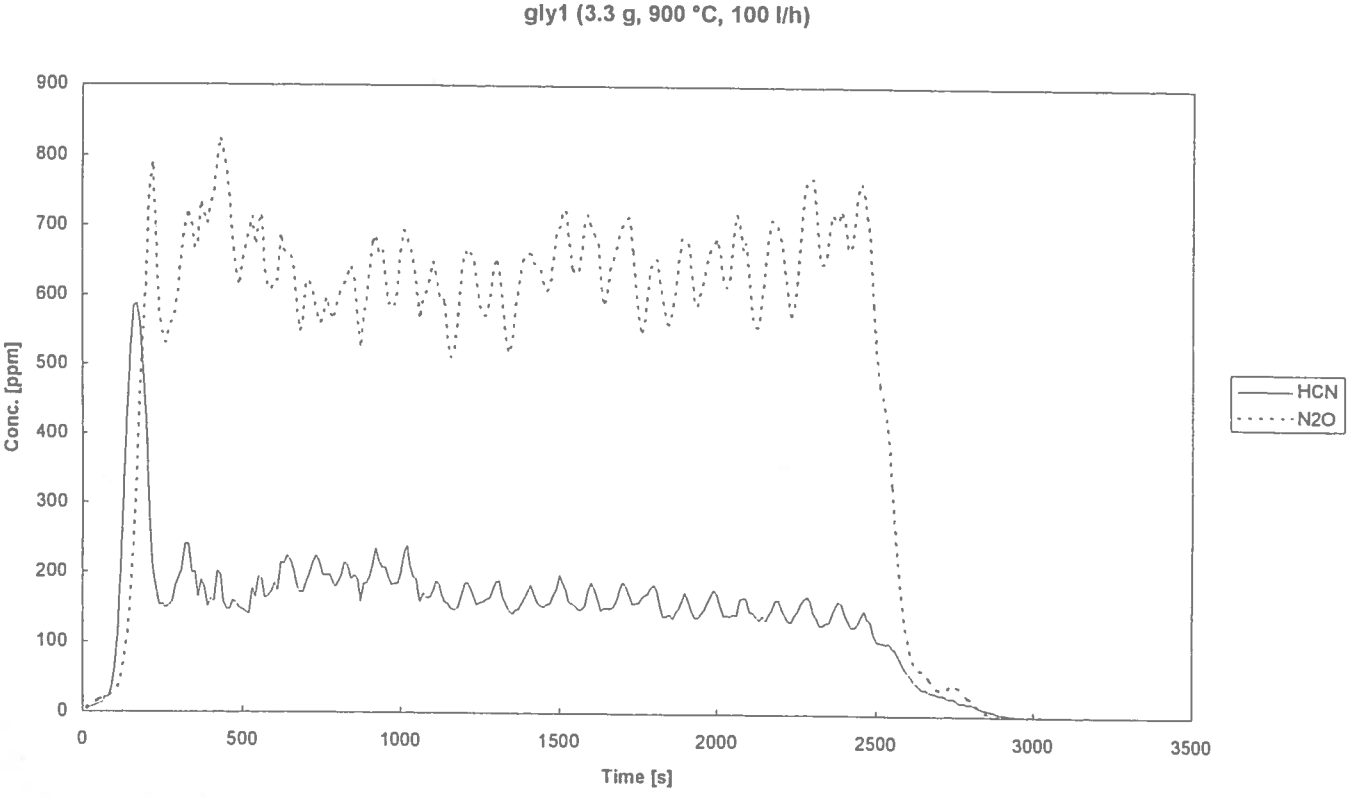

dcb0 (2.2 g, 900 °C, 100 l N2/h)
Conc. [ppm]
Time [s]
CO2
CO
0
10
20
30
40
50
60
70
80
90
0
500
1000
1500
2000
2500
3000

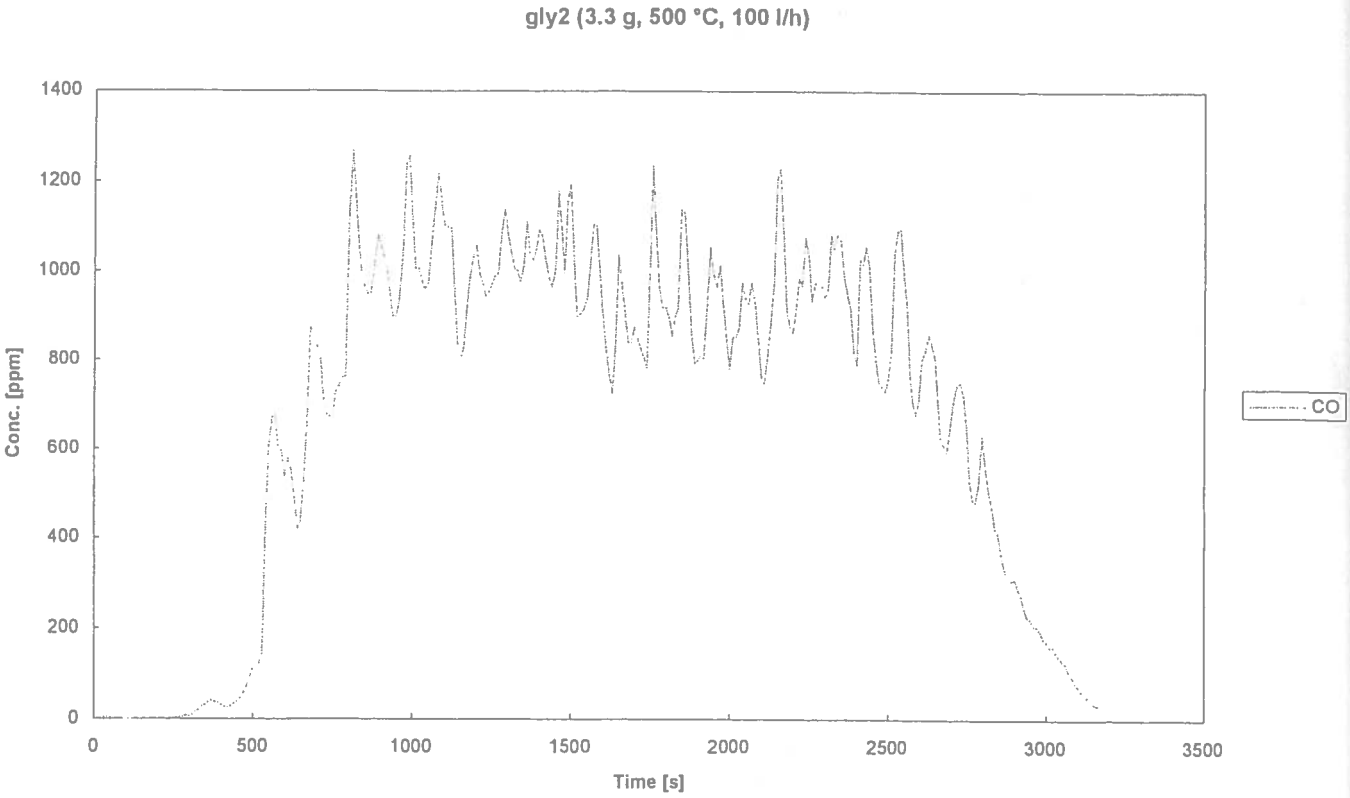
DCB_RES.XLS

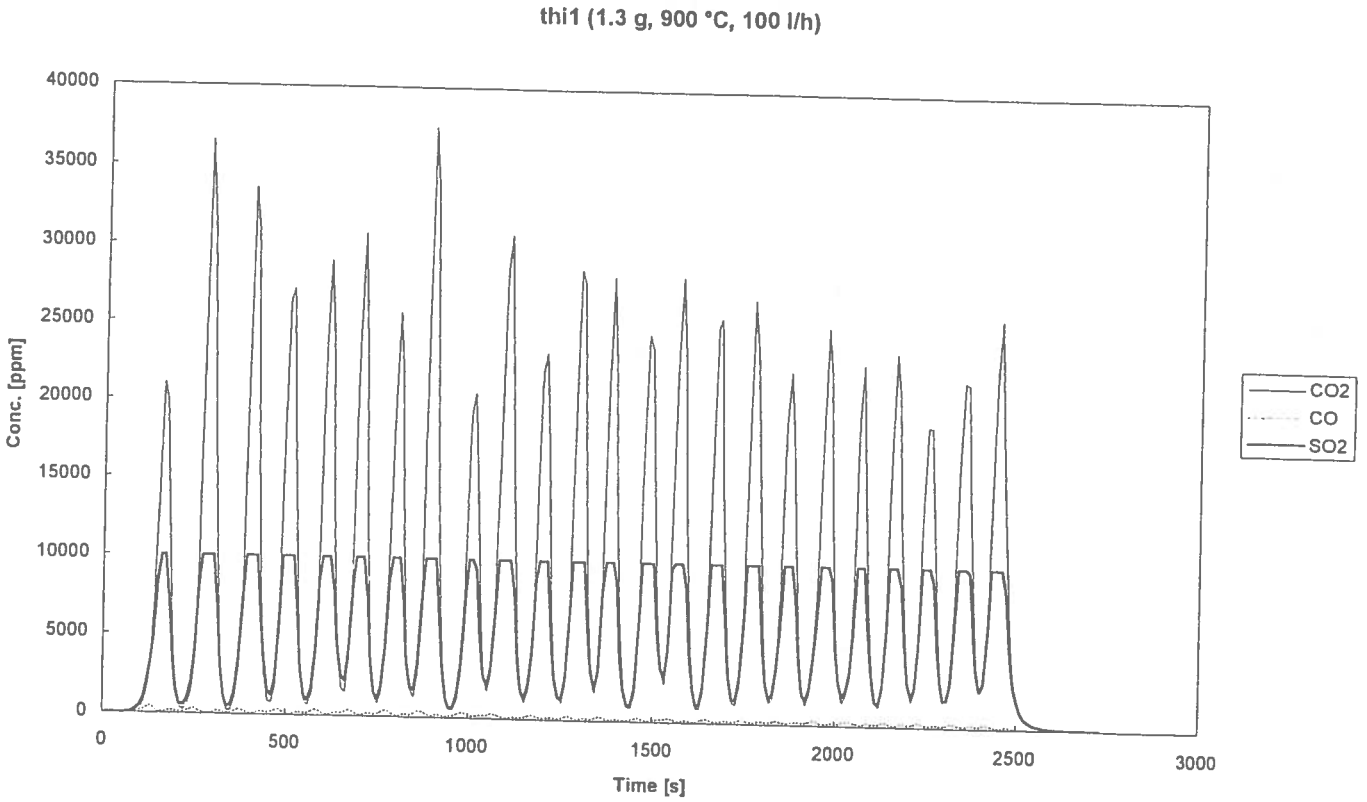

dcb0 (2.2 g, 900 °C, 100 l N2/h)
Conc. [ppm]
Time [s]
HCl
HCN
0
2000
4000
6000
8000
10000
12000
0
500
1000
1500
2000
2500
3000


gly1 (3.3 g, 900 °C, 100 l/h)
Conc. [ppm]
Time [s]
CO2
CO
0
5000
10000
15000
20000
25000
30000
0
500
1000
1500
2000
2500
3000
3500

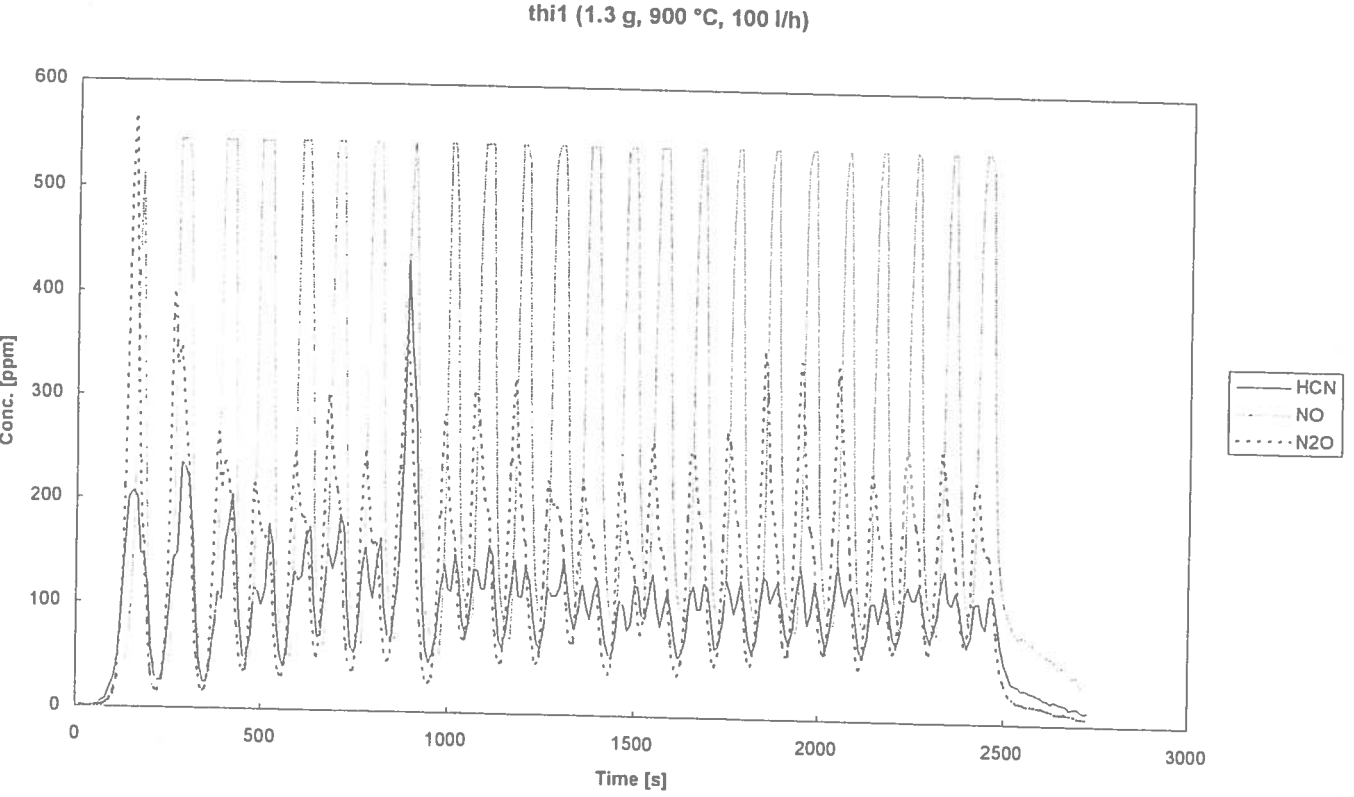
GLY_RES.XLS

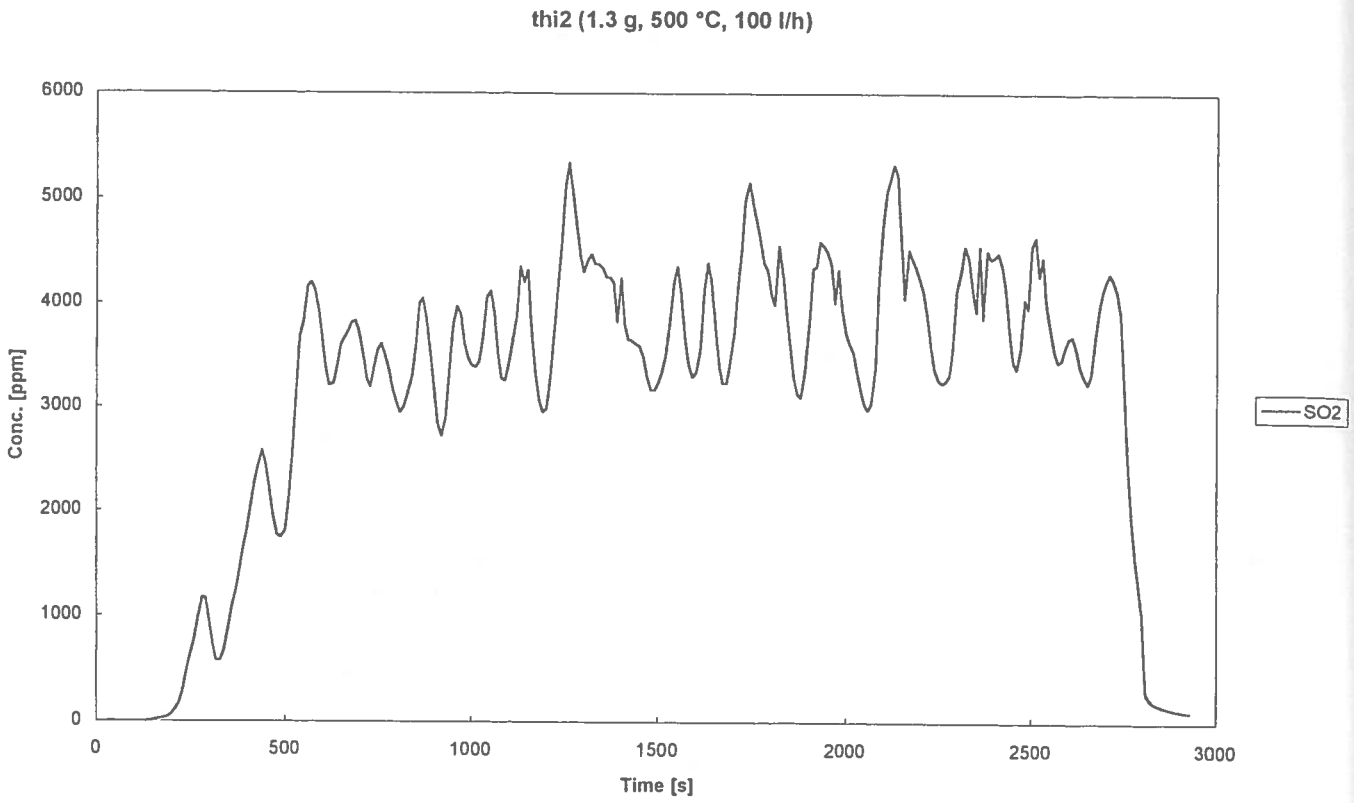

gly1 (3.3 g, 900 °C, 100 l/h)
Conc. [ppm]
Time [s]
HCN
N2O
0
100
200
300
400
500
600
700
800
900
0
500
1000
1500
2000
2500
3000
3500


gly2 (3.3 g, 500 °C, 100 l/h)
Conc. [ppm]
Time [s]
CO
0
200
400
600
800
1000
1200
1400
0
500
1000
1500
2000
2500
3000
3500

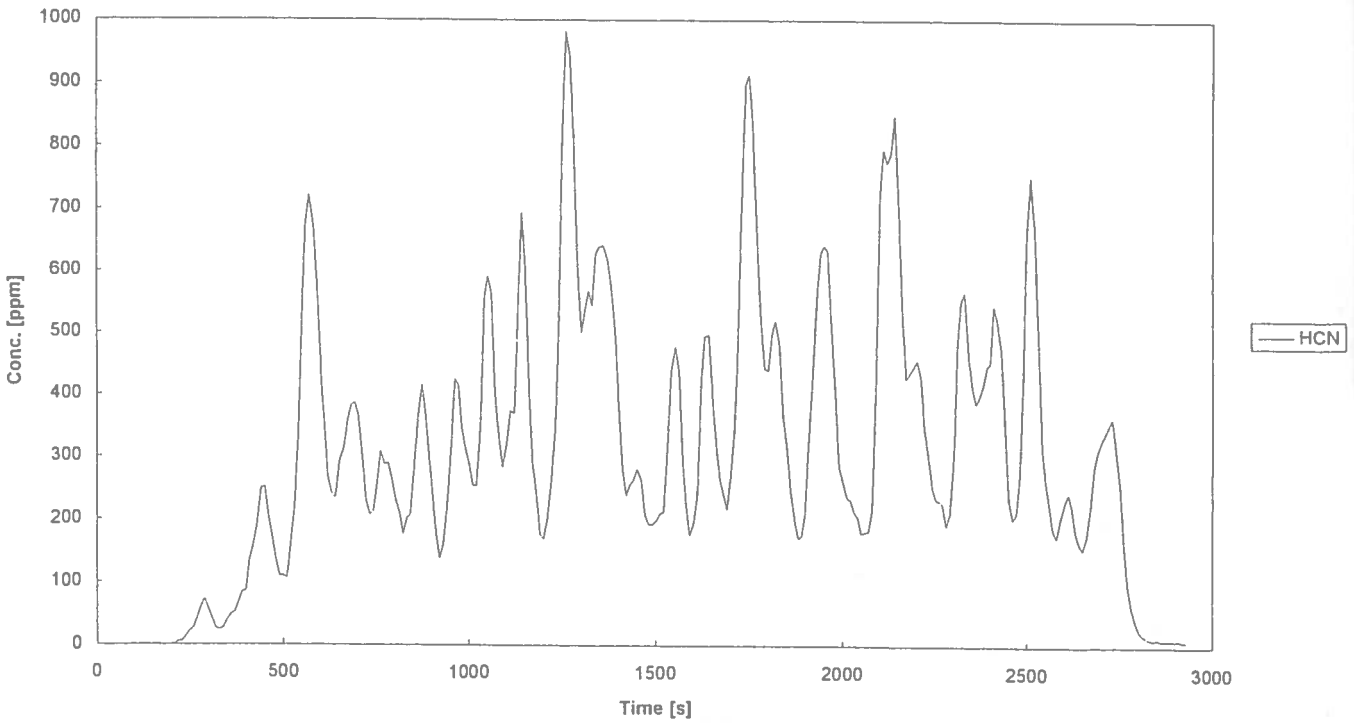

thi1 (1.3 g, 900 °C, 100 l/h)
Conc. [ppm]
Time [s]
CO2
CO
SO2

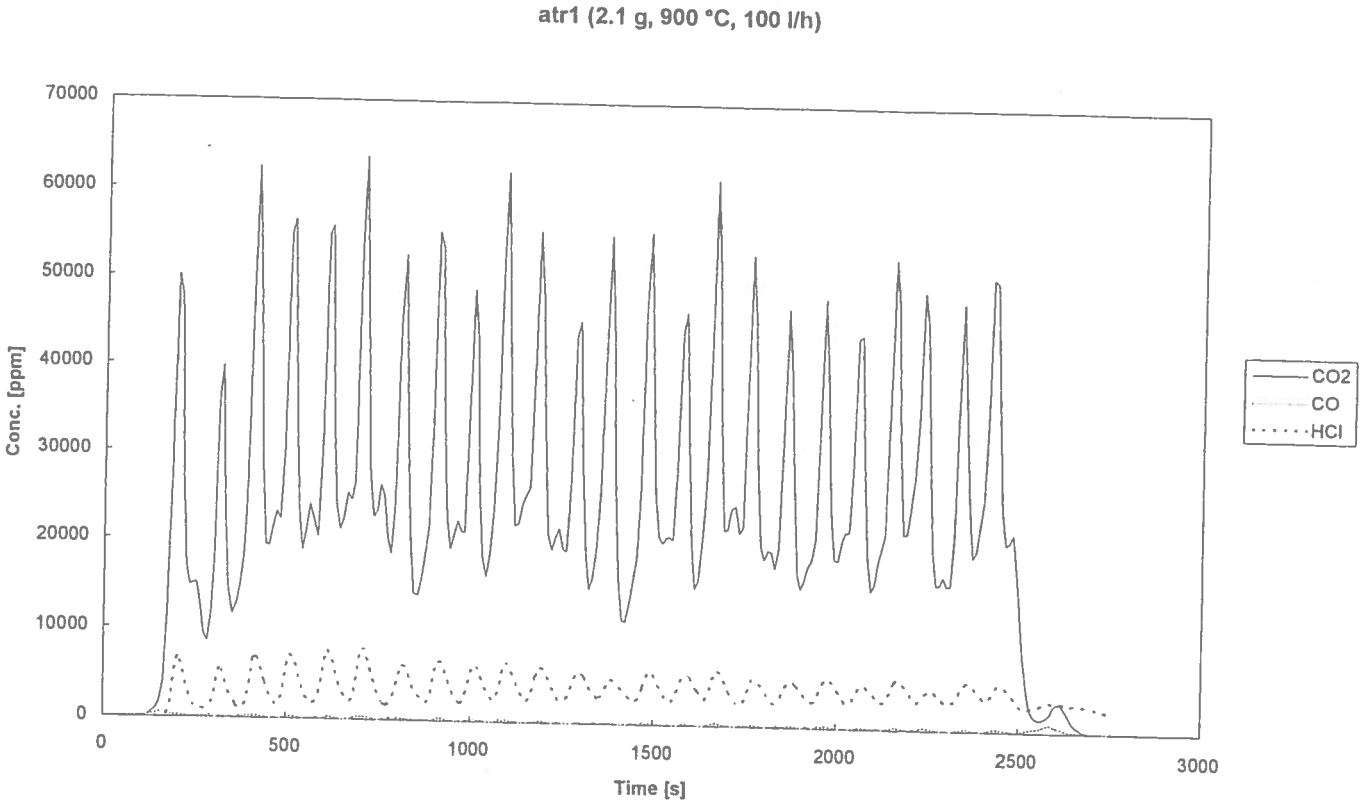
THI_RES.XLS


thi1 (1.3 g, 900 °C, 100 l/h)
Conc. [ppm]
Time [s]
HCN
NO
N2O

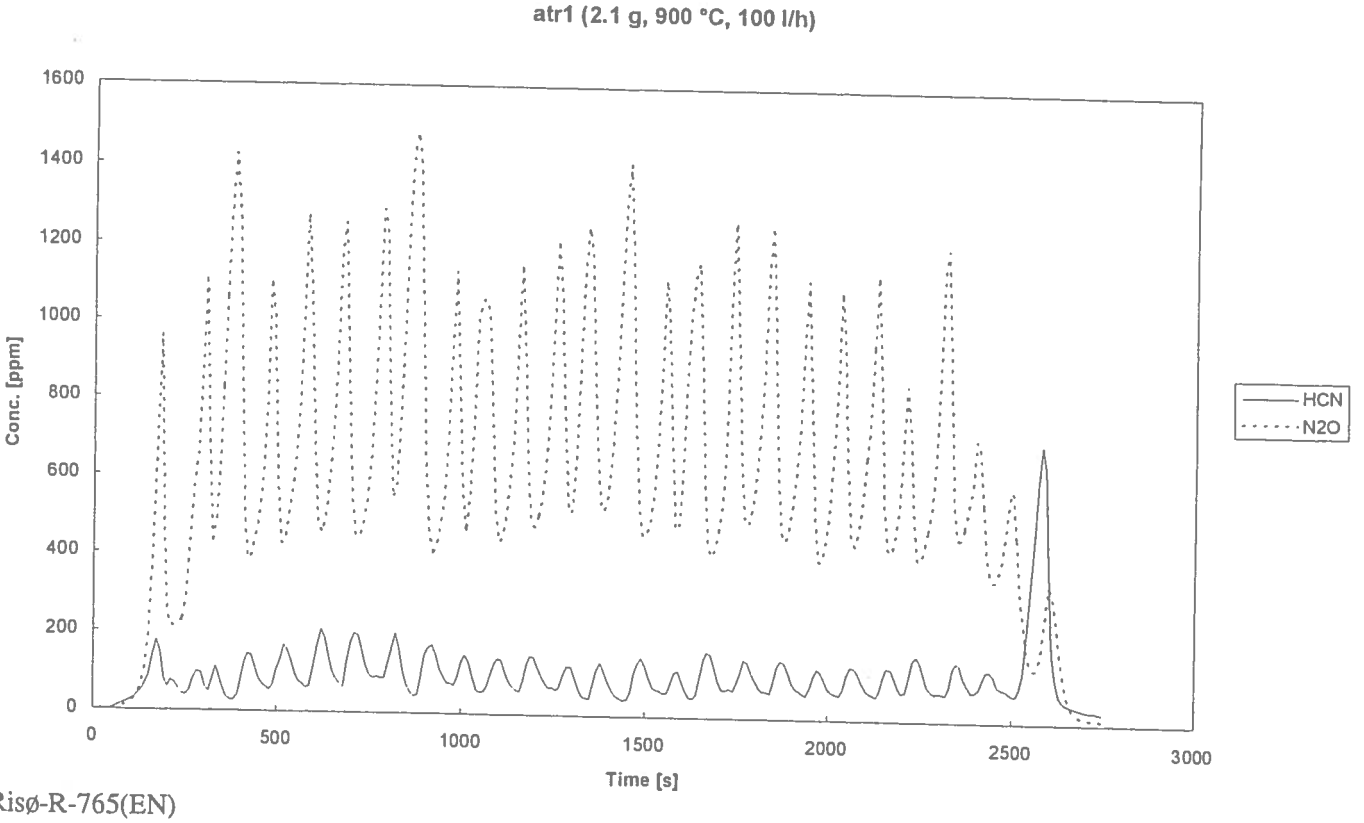

thi2 (1.3 g, 500 °C, 100 l/h)
Conc. [ppm]
Time [s]
SO2
0
1000
2000
3000
4000
5000
6000
0
500
1000
1500
2000
2500
3000

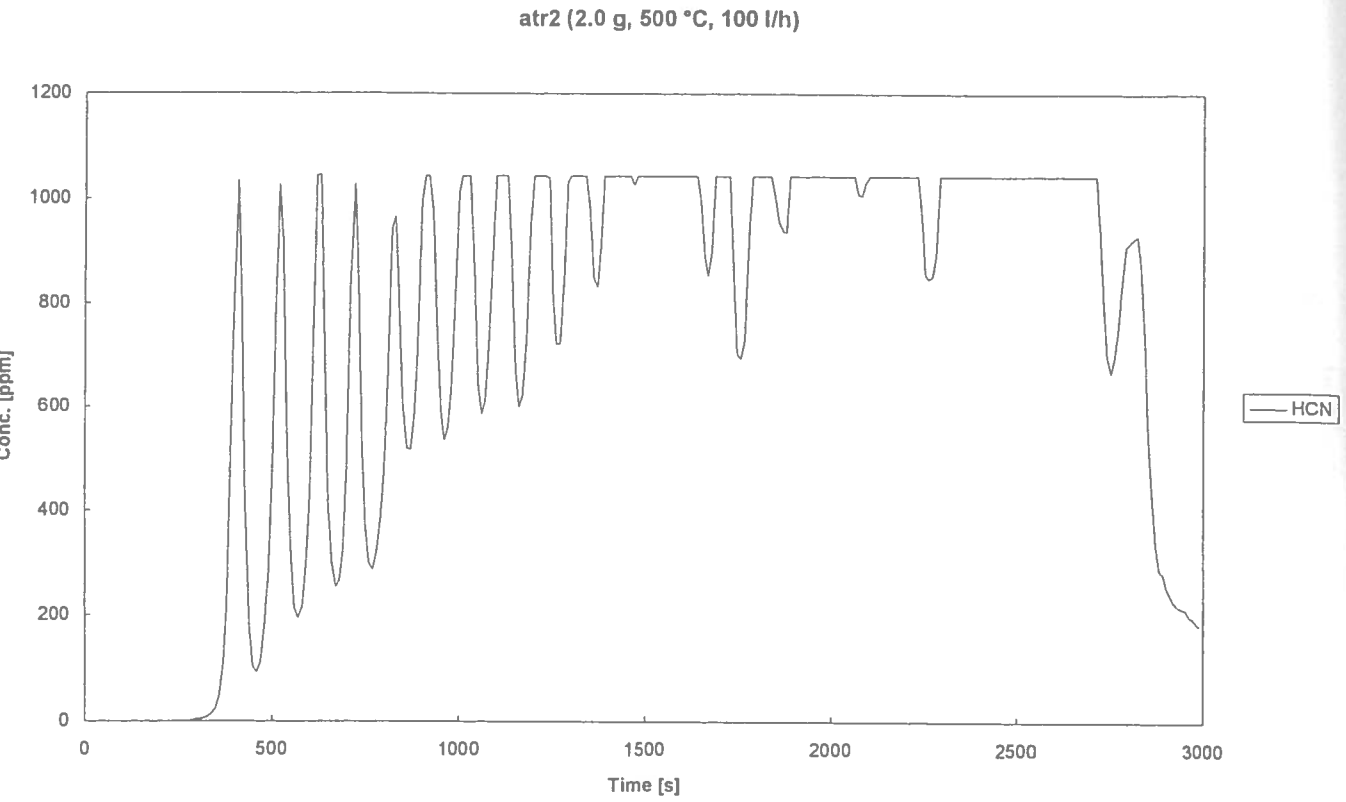
THI_RES.XLS

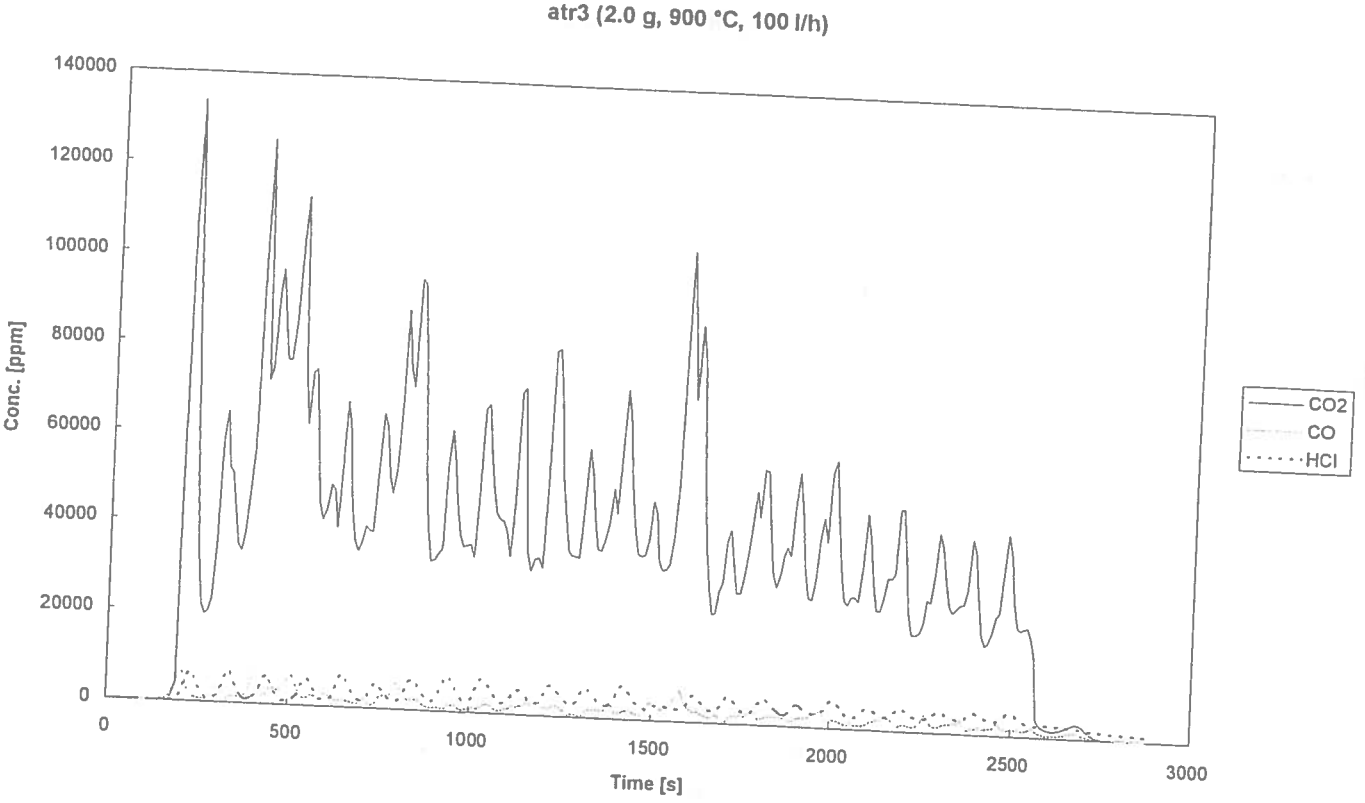

thi2 (1.3 g, 500 °C, 100 l/h)
Conc. [ppm]
Time [s]
HCN
0
100
200
300
400
500
600
700
800
900
1000
0
500
1000
1500
2000
2500
3000


atr1 (2.1 g, 900 °C, 100 l/h)
Conc. [ppm]
Time [s]
CO2
CO
HCl
0
10000
20000
30000
40000
50000
60000
70000
0
500
1000
1500
2000
2500
3000

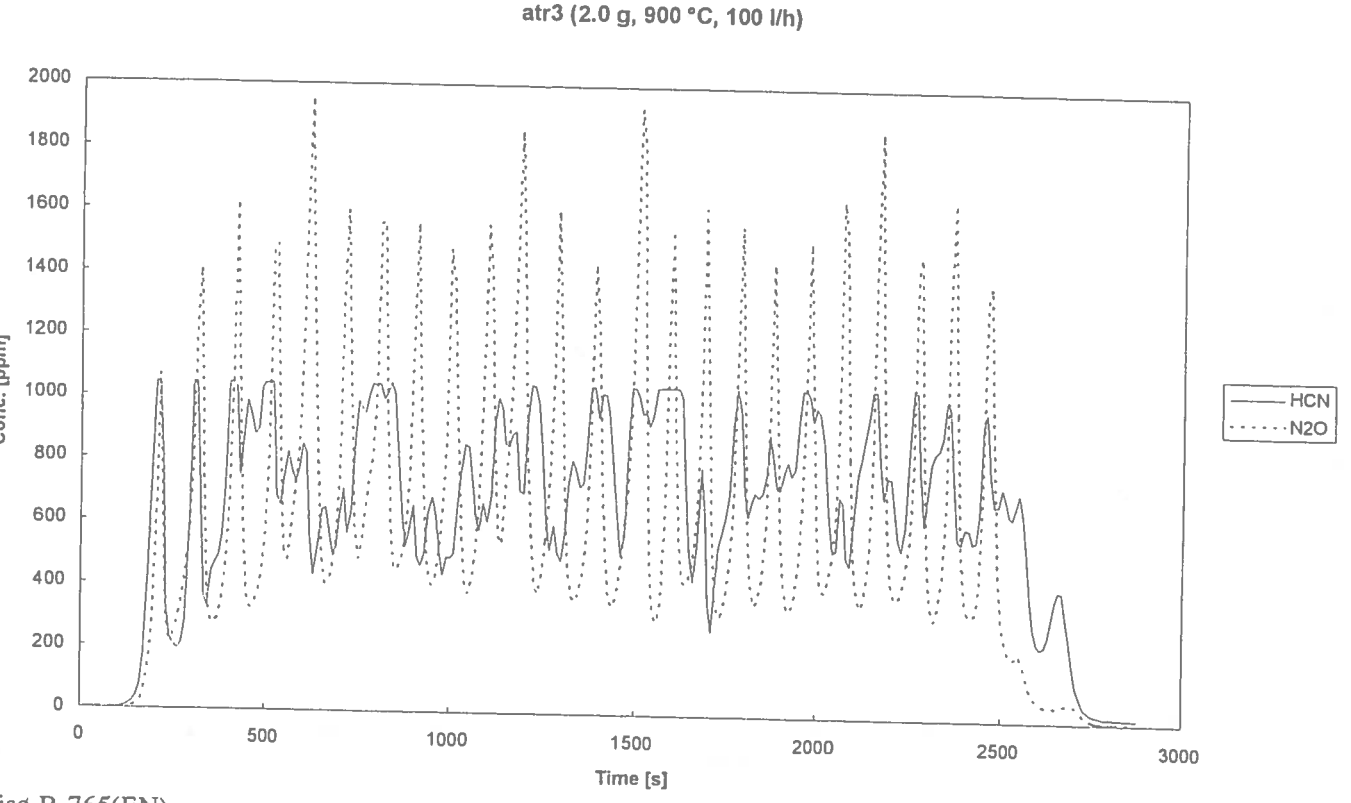
ATR_RES.XLS

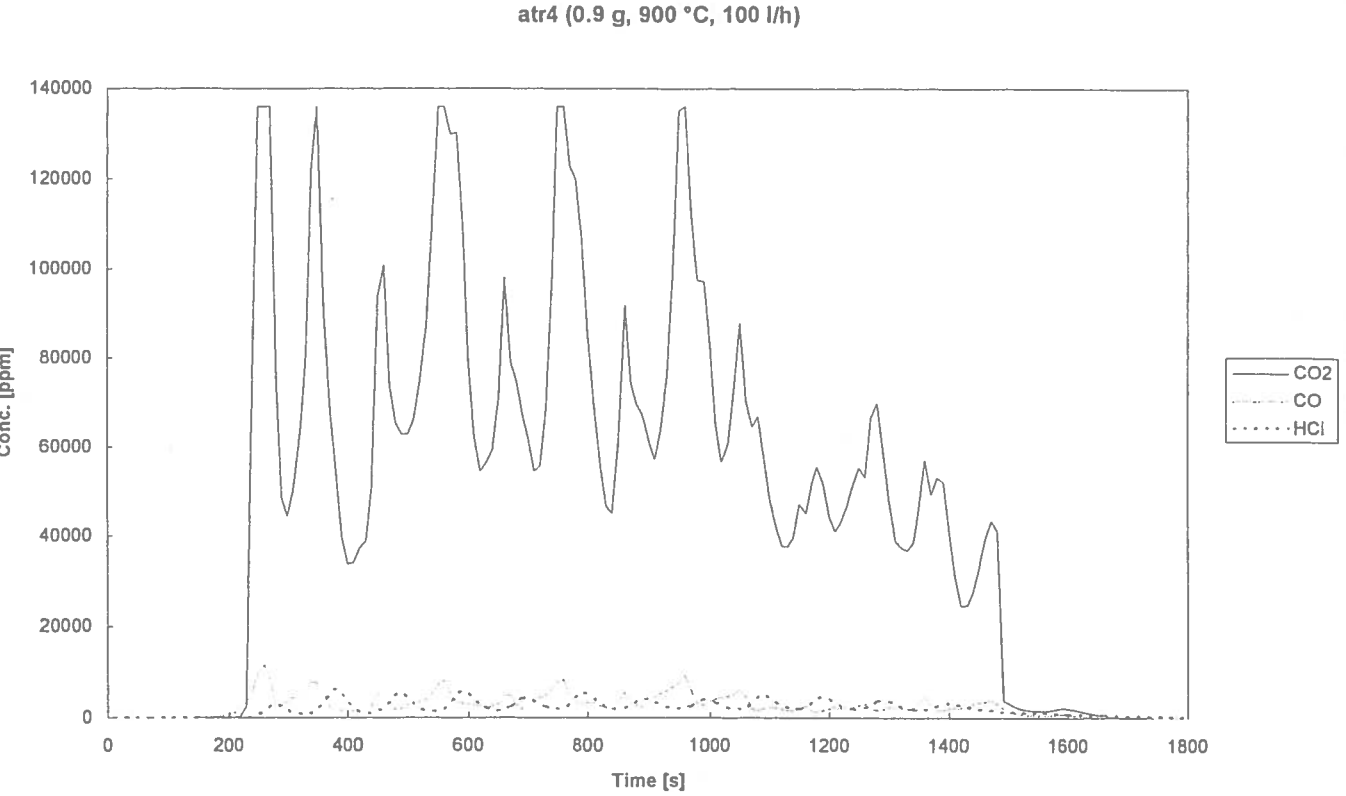

atr1 (2.1 g, 900 °C, 100 l/h)
Conc. [ppm]
Time [s]
HCN
N2O
0
200
400
600
800
1000
1200
1400
1600
0
500
1000
1500
2000
2500
3000


atr2 (2.0 g, 500 °C, 100 l/h)
Conc. [ppm]
1200
1000
800
600
400
200
0
0
500
1000
1500
2000
2500
3000
Time [s]
HCN

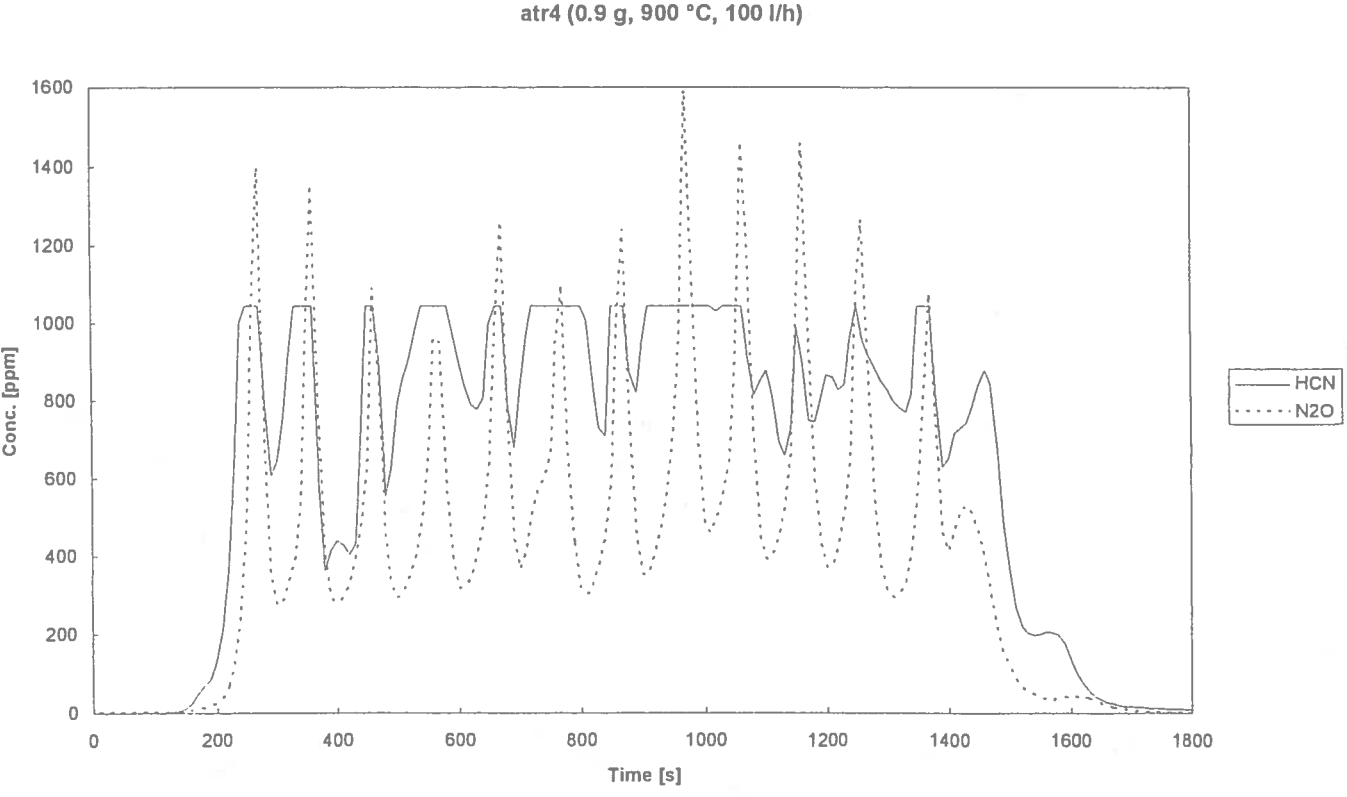

atr3 (2.0 g, 900 °C, 100 l/h)
Conc. [ppm]
Time [s]
CO2
CO
HCl

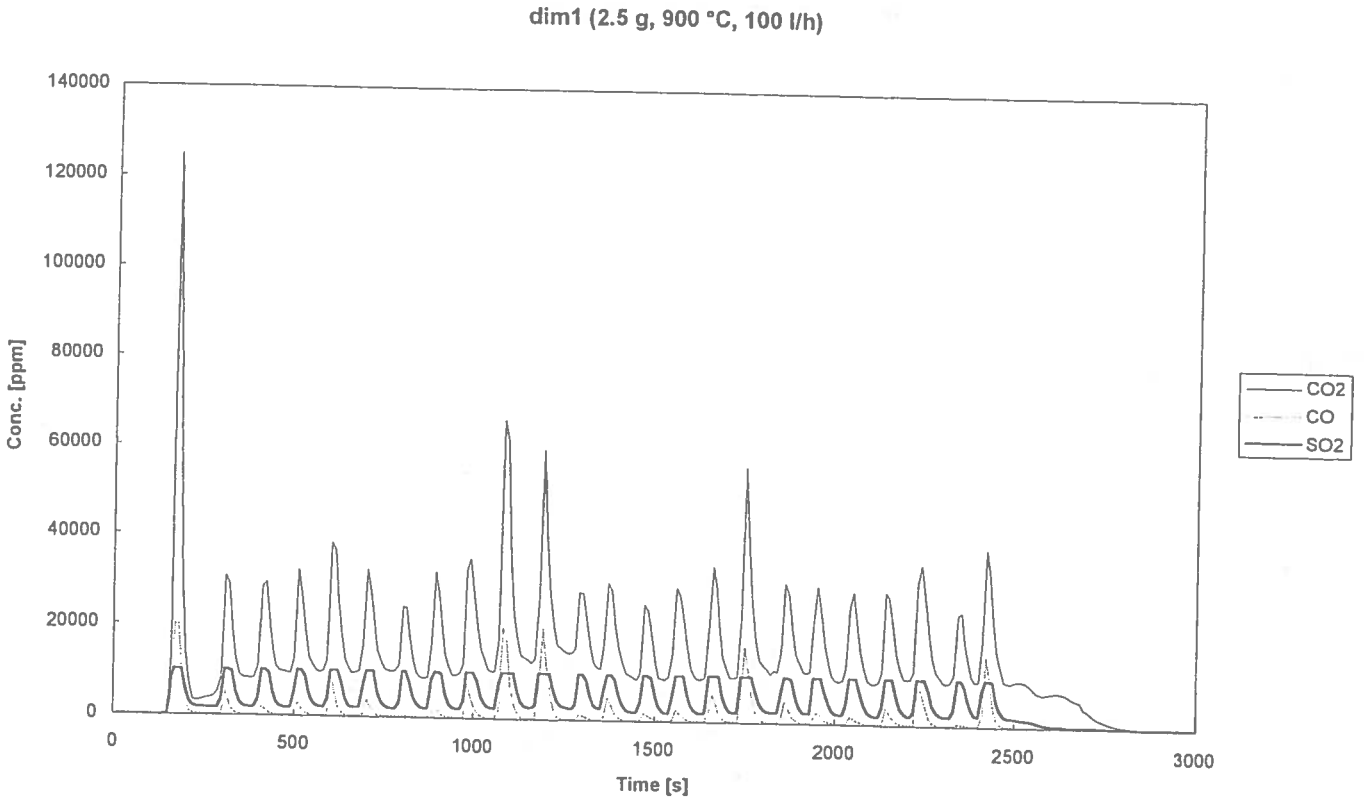
ATR_RES.XLS


atr3 (2.0 g, 900 °C, 100 l/h)
Time [s]
HCN
N2O

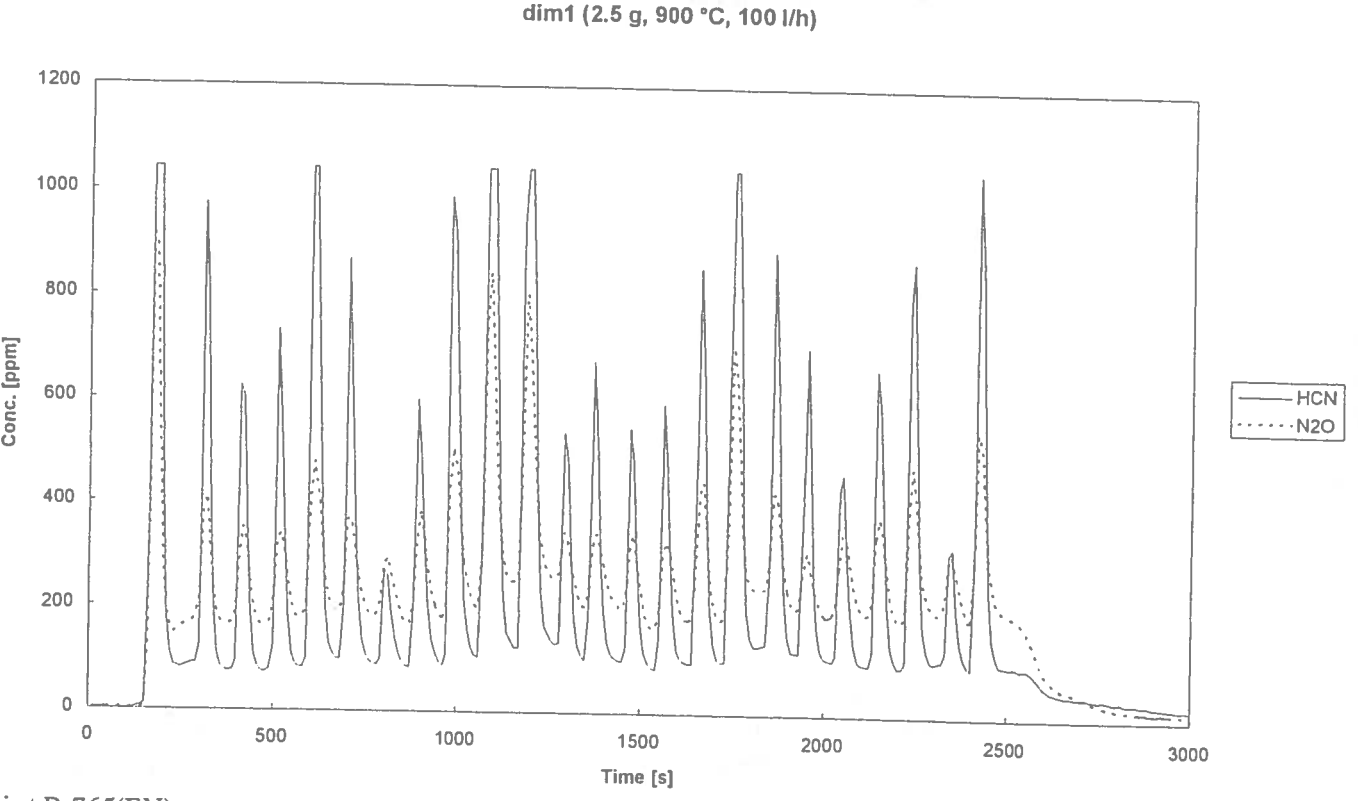

atr4 (0.9 g, 900 °C, 100 l/h)
Conc. [ppm]
Time [s]
CO2
CO
HCl

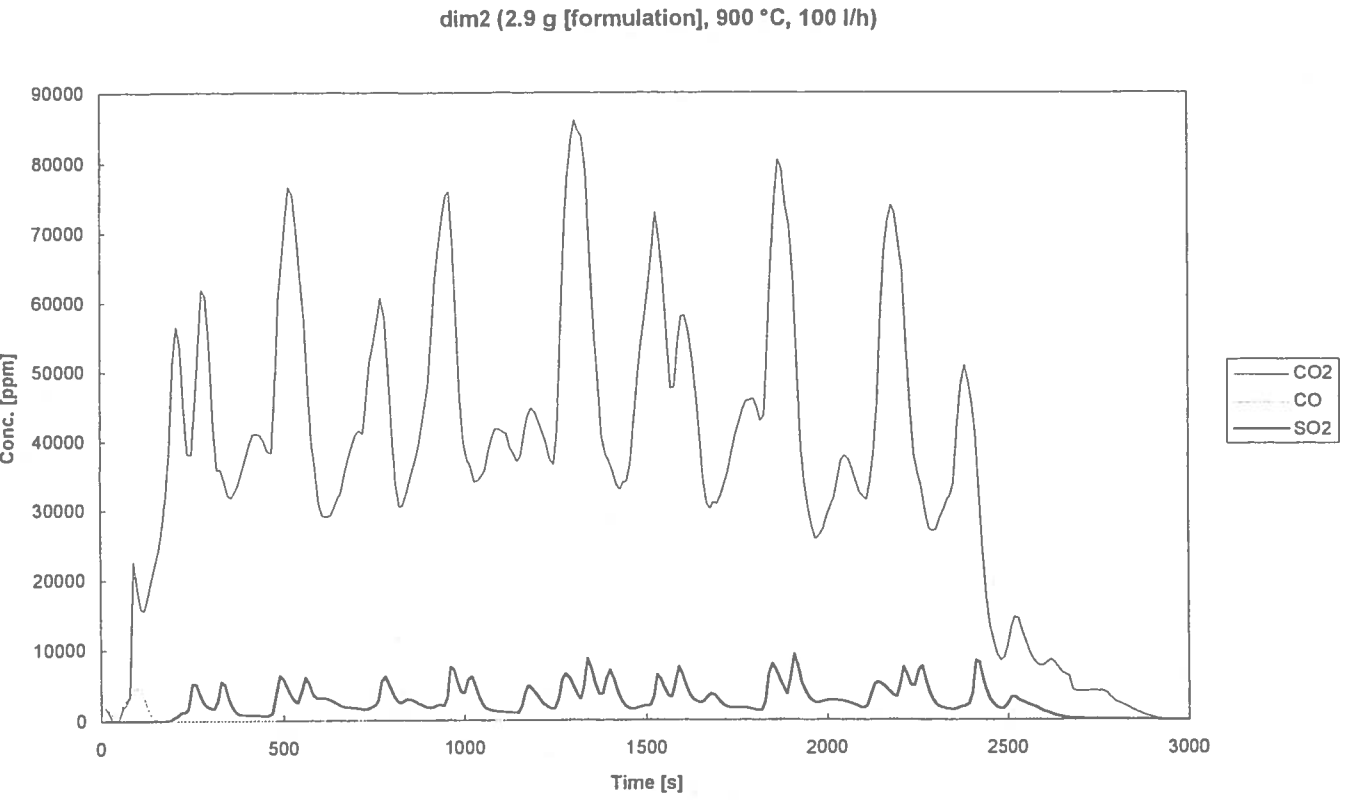
ATR_RES.XLS


atr4 (0.9 g, 900 °C, 100 l/h)
Conc. [ppm]
Time [s]
HCN
N2O

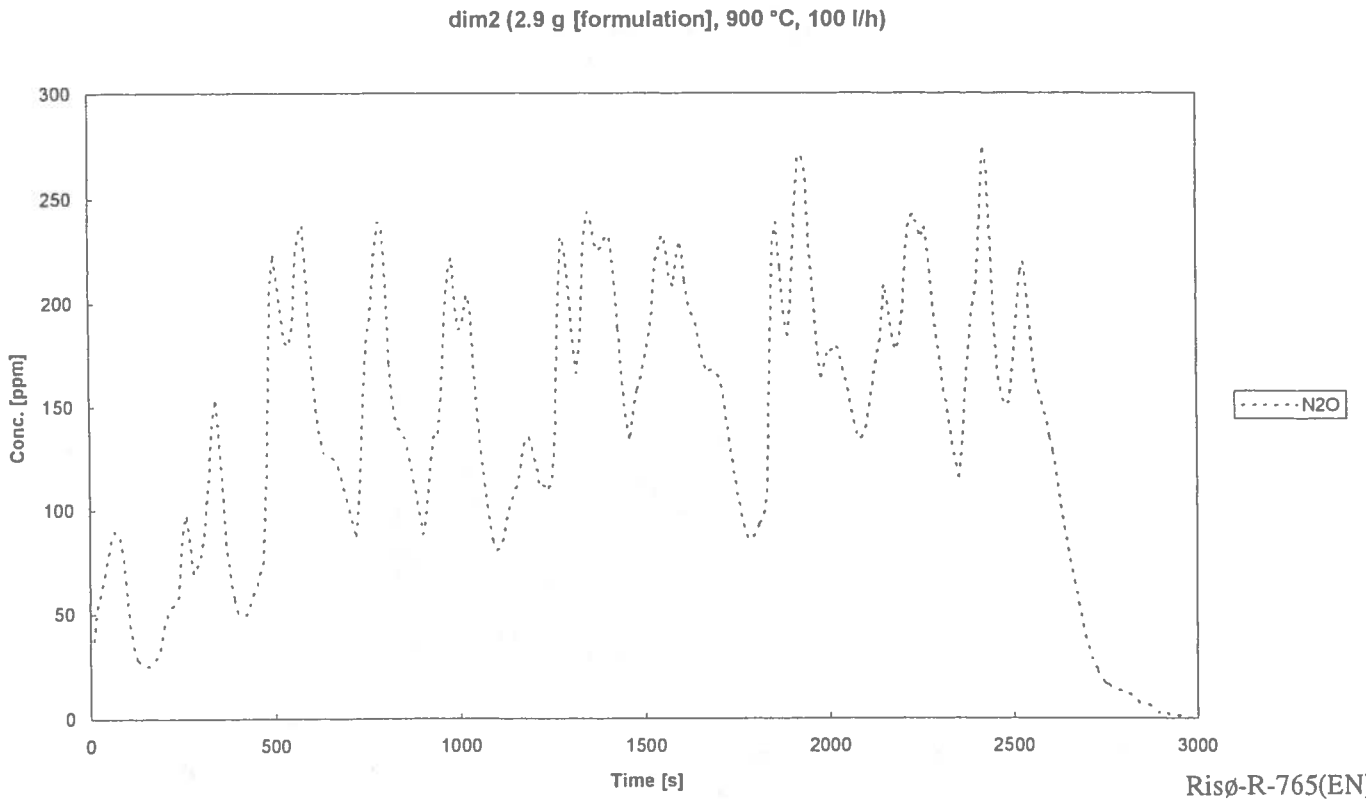

dim1 (2.5 g, 900 °C, 100 l/h)
140000
120000
100000
80000
60000
40000
20000
0
Conc. [ppm]
0
500
1000
1500
2000
2500
3000
Time [s]
CO2
CO
SO2

DIM_RES.XLS


dim1 (2.5 g, 900 °C, 100 l/h)
1200
1000
800
600
400
200
0
Conc. [ppm]
0
500
1000
1500
2000
2500
3000
Time [s]
HCN
N2O


dim2 (2.9 g [formulation], 900 °C, 100 l/h)
Conc. [ppm]
Time [s]
CO2
CO
SO2
0
10000
20000
30000
40000
50000
60000
70000
80000
90000
0
500
1000
1500
2000
2500
3000

DIM_RES.XLS


dim2 (2.9 g [formulation], 900 °C, 100 l/h)
Conc. [ppm]
Time [s]
N2O
0
50
100
150
200
250
300
0
500
1000
1500
2000
2500
3000

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TOXFIRE

Flash Pyrolysis and DIN 53 436 Experiments

Klaus Haahr Jørgensen & Lene Smith-Hansen

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Dept. or group	Date
Systems Analysis	October 1995

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Pages	Tables	Illustrations	References
69	15	9	19

Abstract (Max. 2000 characters)

The report describes microscale experiments carried out by Risø National Laboratory as part of the CEC ENVIRONMENT project "TOXFIRE. Guidelines for Management of Fires in Chemical Warehouses". The objective of the project is to develop the basis for two sets of guidelines in relation to fires in chemical warehouses: Guidelines for the safety engineers to be used in accident prevention and guidelines for the fire brigade to be used if an accident nevertheless occurs.

A screening of 30 compounds (mainly pesticides) has been carried out by use of combined flash pyrolysis-GC/MS. The pyrolysis products have been identified and compared with literature data as well as with previous combustion experiments.

DIN 53 436 combustion experiments have been carried out with six pesticides: Lindane, dichlobenil, glyphosate, thiram, atrazin and dimethoate. Experiments have been carried out at 500 and 900 °C at varying oxygen concentrations, flow rates and sample load. The concentrations of combustion gases (CO_2, CO, $COCl_2$, HCl, HCN, SO_2, NO, N_2O etc.) have been measured on-line by use of FTIR and the total yields determined.

Descriptors INIS/EDB

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RISØ

Objective

The objective of Risø's research is to provide industry and society with new potential in three main areas:

- *Energy technology and energy planning*
- *Environmental aspects of energy, industrial and plant production*
- *Materials and measuring techniques for industry*

As a special obligation Risø maintains and extends the knowledge required to advise the authorities on nuclear matters.

Research Profile

Risø's research is long-term and knowledge-oriented and directed toward areas where there are recognised needs for new solutions in Danish society. The programme areas are:

- *Combustion and gasification*
- *Wind energy*
- *Energy technologies for the future*
- *Energy planning*
- *Environmental aspects of energy and industrial production*
- *Environmental aspects of plant production*
- *Nuclear safety and radiation protection*
- *Materials with new physical and chemical properties*
- *Structural materials*
- *Optical measurement techniques and information processing*

Transfer of Knowledge

The results of Risø's research are transferred to industry and authorities through:

- *Research co-operation*
- *Co-operation in R&D consortia*
- *R&D clubs and exchange of researchers*
- *Centre for Advanced Technology*
- *Patenting and licencing activities*

To the scientific world through:

- *Publication activities*
- *Co-operation in national and international networks*
- *PhD- and Post Doc. education*

Key Figures

Risø has a staff of just over 900, of which more than 300 are scientists and 80 are PhD and Post Doc. students. Risø's 1995 budget totals DKK 476m, of which 45% come from research programmes and commercial contracts, while the remainder is covered by government appropriations.

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